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THE EFFECTS OF IONS IN COLLOIDAL SYSTEMS

THE EFFECTS OF IONS IN COLLOIDAL SYSTEMS

BY

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BALTIMORE

WILLIAMS & WILKINS COMPANY

1925

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Made in United States of America

Published March, 1925

COMPOSED AND PRINTED AT THE
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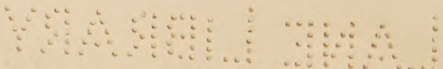
BY THE WILLIAMS & WILKINS COMPANY
BALTIMORE, MD., U. S. A.



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PREFACE

I had the honor of being invited to give some lectures by several universities of the United States of America during April and May, 1924. These invitations were initiated by Prof. Jacques Loeb of The Rockefeller Institute for Medical Research in New York and came from the University of California, Berkeley, Cal.; Leland Stanford University, Cal.; University of Chicago, Chicago, Ill.; University of Pennsylvania, Philadelphia, Pa.; Johns Hopkins Medical School, Baltimore, Md.; Yale University, New Haven, Conn.; and The Rockefeller Institute for Medical Research, New York. At the same time I had the privilege of adressing in Washington a united meeting of the National Academy of Science and the American Chemical Society. I have gathered the material of these different lectures which I am presenting in this monograph.

I appreciate very much the opportunity afforded me by the institutions above mentioned. To my deepest regret the sudden death of Prof. Jacques Loeb just before my arrival in America prevented me from expressing my thanks to this unreplaceable scholar personally.

A quite special thanks is due to the Aichi Medical University in Nagoya, Japan, which granted me the leave of absence for my trip to America, in a most generous manner.

I am very much obliged to Dr. W. A. Perlzweig, Johns Hopkins Medical School, for his kind revision of my English text.

THE AUTHOR

INTRODUCTION

Biological investigations may be directed toward quite different goals. The tendency of most of those investigators before whom I have the honor of discoursing is to elucidate the qualities and alterations of the living matter by reducing them, as far as possible, to those natural laws known in chemistry and physics, without having recourse to forces unknown in the inanimate world. Though this endeavor is not the only possible one for a biologist, and though it is confined by natural limits, yet it seems to me most fertile of all in the present period of biology. The general tendency of this kind of investigation is *application* of the laws of physics and chemistry to biological subjects. If you take that literally, it would not be necessary for a biologist to take part himself in propagating and amplifying the very laws of physics and chemistry but only to find out by which manner they may be *applied* to biology; just as a builder of a steam engine need not amplify the theory of thermodynamics but only apply it. This point of view is widely spread but seems to me not to be justified. Since no problem of physical chemistry has finite limits nor is completely exhaustible, any investigator will exhaust a problem at the best in a direction adequate

to his interests. We should not expect physical chemists to prepare and elaborate a problem ready for application in such a manner that biologists need only seize them and apply. I consider it as one of the most essential missions of biologists to amplify or at least to organize those branches of physics and chemistry in those directions which are likely to be available to physiological problems. Many physiologists display a certain bias toward considering these endeavors as not belonging to physiology. But I do not agree with this tendency. It does not matter at all that, temporarily, a physiologist abandons the experiments on living subjects and restricts himself to experiments with inanimate things. To be sure, that is not to be our final aim, but the detour will be worth while. Therefore, consider this series of lectures as an essay in promoting those branches of physical chemistry which physiologists may expect to be the key to the rôle of electrical and colloidal phenomena in living matter. Of course, do not expect too much from a biologist who is talking about physical chemistry. We cannot be compared to those ingenious physicists upon whose shoulders we are standing. Our work will chiefly consist of a compilation and a gathering of facts and theories known before, a compilation nevertheless with a definite aim, that is: fitness for application to biology. I think such a study is an essential part of biology, in fact, an indispensable

part of it and not even a detour; but the most direct and best way.

Among such problems, the effect of ions in electrifying surfaces and in influencing the conditions of colloidal systems is nowadays a very important one. So I chose it as the subject for my lectures, beginning with a review of *adsorption of ions* in the widest meaning of the word. For introduction, I should like to start from some general remarks on adsorption.

THE EFFECTS OF IONS IN COLLOIDAL SYSTEMS

I. SOME GENERAL REMARKS ON ADSORPTION

First of all I wish to explain how I shall use the word *adsorption*, because it is used with different meanings. Some authors especially emphasize adsorption to be a process which takes place on a surface. Others use it rather in the sense of antithesis to chemical combination. In the following lecture I take adsorption to mean only the phenomenon where some substance homogeneously dissolved in a phase accumulates at the boundary layer to a higher concentration or aims at some regular arrangement of its molecules in the boundary layer, no statement being made whether this process is based on physical or so-called chemical forces. The definition of the other conceptions used here may be given by an example. When a solution of acetone in water is shaken with charcoal, acetone is partly found to be concentrated on the surface of the charcoal. Experiments cannot decide whether the molecules of acetone are in a direct molecular combination with the molecules of charcoal, or whether the molecules of acetone only accumulate

in the superficial layers of the water. Besides it should be of no account to the following considerations whether charcoal, in consequence of its chemical nature, itself participates in adsorption or whether it only acts by enlarging the surface of the water. Let us define such a phenomenon under the term of adsorption, and let us consider charcoal as the adsorbing medium or the adsorbent, and acetone as adsorbendum or adsorbate. This definition has a peculiar and strange consequence. According to the principle of Gibbs, at the free surface of an acetone solution, at its boundary surface against the air, a relatively massless space, there is an accumulation of acetone because acetone diminishes the surface tension. In this case we would have to call the air, or the nearly empty space, the adsorbent. Since it is only the question of a formal definition, one should put up with this somewhat unusual consequence of the definition. You will recognize later that this uniform definition leads to an essential simplification in explaining the whole matter. Suppose it were important in a single case to emphasize the inactivity of such an adsorbent as the air or the vapor, we might call that "apparent adsorption" in opposition to a "real" one. These conceptions being fixed I should like to speak today about adsorption of ions.

In some of my papers I emphasized the fact that there is a gradual transition from a definitely chemi-

cal affinity to a feeble attraction like adhesion in certain adsorption phenomena. Nevertheless Bayliss, who generally propagates the same idea, has succeeded in obtaining two kinds of compounds of alumina with congo red of different colors, the one of which may be designated as an adsorption combination, the other as a real salt. Indeed Bayliss emphasizes the impossibility of discriminating between adsorption and chemical combination in any case, but in single cases he was able to discriminate between two kinds of combination for the same components. For this reason he denies the validity of my representation of adsorption. It is very interesting to investigate how this divergence of opinions could arise and be maintained.

A very instructive example in this respect is the one given by Bayliss, that the adsorption of congo red by pure filter paper is increased by neutral salts, even by such neutral salts as NaCl which do not give any insoluble salt with congo red by exchange of the cations. On the other hand, Rona and I pointed out that the adsorption of congo red by pure filter paper depends on the calcium content of the paper and takes place only in such a degree as a calcium compound of congo red can be formed. The explanation of this contradiction is most instructive and is given by the following consideration.

In my investigations of adsorption I have restricted myself to such cases where the adsorbate

was given in the form of a true solution with no properties of a colloidal condition. I emphasized the fact that the identification of adsorptive forces and definitely chemical affinity only holds if the adsorbent has the chemical character of an electrolyte, or better, of a heteropolar compound, such as silicates, metal hydroxides, mastic, proteins, etc., and if the adsorbate is given as a true solution. If the adsorbent is a material of electro-indifferent character, adsorption of truly dissolved substances is extremely small as a rule, in opposition to the general opinion, except in the case of some kinds of charcoal. I shall return to this problem of charcoal in a special chapter. But I also emphasized that the conditions are changed in a striking manner if the adsorbate is present in the form of an evidently colloidal state. In this case, a general attracting power of any surface for colloidal micellae seems to exist which can be modified by electrical charges. If the adsorbing surface has an electrical charge of the opposite sign to the micellae, adsorption is increased, if the sign of charge is equal, adsorption is decreased or even annulled. The more a dye-stuff is colloidal the more generally there is an adsorbability at a surface of any chemical constitution which is influenced only by the sign and the magnitude of the electrical charges but does not depend on the possibility of the formation of an insoluble real salt. In such a case, the difference

between a chemical combination and an adhesion or adsorption is most pronounced. Now, for a dye-stuff like picric acid which has no inclination to form a colloidal state the rules given by me hold absolutely. Congo red forms however a nearly true solution only in a quite salt-free solution, such as I used in my investigations on adsorption by filter paper. According to Bayliss' investigations, these rules do not hold for solutions of congo red containing NaCl. For this salt increases the adsorption of congo red, though the sodium salt of congo red is soluble. But congo red is decidedly colloidal in aqueous solution when NaCl is present, and the colloidal *micellae* of congo red are adsorbed by any surface provided the electrical charges do not prevent the particles from adhesion to the second phase. I then expressed my intention to continue my investigations of adsorption for the case of a colloidal state of the adsorbate and I will certainly do so some day. At present I only wish to emphasize that the observations of Bayliss do not influence my considerations of adsorption in *true solutions*.

Today we are dealing particularly with adsorption of ions, and here we may apply the rules of adsorption in true solutions.

II. ELECTRIC PHENOMENA PRODUCED BY THE ADSORPTION OF IONS

Adsorption of ordinary unelectrical molecules may only be proved by chemical analysis and cannot be proved when it takes place to so slight an extent that the alterations of concentration may no longer be detected by chemical analysis. Only for certain electroneutral molecules, which possess a very strong capillary activity, adsorption may sometimes be proven when other methods of chemical analysis are insufficient, by measuring the alteration of the surface tension. In opposition to that, the adsorption of an ion may be easily proved in any case even if the adsorption cannot be demonstrated by chemical analysis. This is due to the fact that the ions produce *electrical* phenomena. Electrical charges may be also produced by free electrons, not only by ions, but we are justified in neglecting any effect of free electrons in the solution given in our experiments in which we have no free metals. So, at least in our cases, we may assert that any electrical charge of a surface means adsorption of ions. Let us see if it is possible to justify this assumption.

The electrical phenomena by which we perceive the adsorption of ions are of two kinds, firstly *elec-*

tromotive forces, and secondly cataphoresis, electro-endosmosis, etc., comprised in Freundlich's terms as *electrokinetic* phenomena. Among the electromotive forces let us only consider, in very few words, those arising at non-metallic surface layers, because in the case of metals we should take into account also free electrons, and this case has little direct relation to biological phenomena. We can construct electric chains without metals, as shown by the studies of Nernst, Haber, Beutner and others. In these cases, the difference of the potential to be considered is the one between any place within the one phase and any place within the other phase, provided these places are at a sufficient distance from the boundary phase. A distance of almost ultramicroscopical order of magnitude may be generally considered as at sufficient distance in this respect. In contrast to that, in electrokinetic phenomena the effective potential difference is the one between the fluid and movable part of one phase and the fixed part adherent to the boundary surface of the *same* phase. Thus, regarding the entire change of the potential from the interior of the one phase to the other phase, the whole difference of potential is effective for the electromotive force, when this boundary phase is the one pole of a galvanic chain without metals. But only a part of this potential difference is effective, or at least, may be effective for electrokinetic phenomena. This idea has been for the first

time developed by von Smoluchowsky and then especially by Freundlich. It involves the idea that the drop of the potential at a boundary surface might not be a discontinuous one, as was usually supposed, but there is a gradual transition from the one potential to the other. Nay, any course whatever of the potential curve within the boundary layers is admissible, even with change of sign. Such a course of the potential has not any influence on the potential effective for electromotive forces, but it has on the force effective in cataphoresis and endosmosis. In consequence of that we must not expect that a potential difference of a boundary surface measured by some electrometric method, should be always equal to the potential difference calculated from cataphoresis data. This consideration has been emphasized especially by Freundlich and seems to me to be most useful. We should take care however not to exaggerate it by the assumption, that in any case the potential difference effective in a surface phenomenon necessarily must be different from the potential difference effective in electromotive forces. It seems to me that only when strongly adsorbable ions are present, the discrimination of these kinds of potential differences has a measurable practical meaning. May I be allowed to recall the fact that we measure the absolute zero point of a mercury electrode by investigating the conditions for the maximum of surface tension of

a mercury meniscus, and, after all we know about this problem, this determination of the absolute value of the potential of mercury from a *surface* phenomenon may be applied for the potential of the mercury which forms the one pole of a galvanic chain, too; provided the surface tension is measured against such solutions, which contain no strongly adsorbable ions. Though this problem requires a special investigation, yet I am mentioning it now for a reason which will be made clear later on.

Electrokinetic phenomena are for the most part known for as long a time as the electromotive phenomena of the Volta chain. They are chiefly electrical endosmosis, electrical cataphoresis and hydrodynamic potential ("Strömungspotentiale"). The phenomena concerning the stability of colloidal solutions should also be reckoned with these. Electrical endosmosis occurs when an electric current passes through a tube filled with a solution of electrolytes and the path of the current is interrupted by a diaphragm of a compressed powderlike substance. By the effect of the applied potential fall water is pressed through the pores of the diaphragm. If the solid powder is not compressed to a diaphragm but freely suspended in the water, for instance in form of a colloidal solution, on the contrary, the suspended particles are moved against the liquid, that is called electrical cataphoresis. When forcing an electrolyte solution by hydrostatic pressure through a glass

capillary, the ends of the capillary show an electrical potential difference against each other. That is hydrostatic potential. Among these phenomena cataphoresis has the nearest relation to the electrical phenomena in colloidal solutions; so let us confine ourselves chiefly to this phenomenon.

The theory of cataphoresis is essentially based on Helmholtz' ideas. He admitted that an electrical double layer is formed at the surface of the solid particles; he considered each of both layers as a real surface in the mathematical sense, and a solid particle suspended in a liquid and surrounded by an electric double layer has a certain similarity to an electrical spherical condenser. And so one may define the following quantities: electrical density; the distance of the two layers from each other; and the potential difference of the two layers. The surface density being given, the potential difference of the two layers is proportional to their distance. Helmholtz pointed out a relation between the potential of the double layer and the velocity of the electrical cataphoresis under the influence of an electric field. This relation can be expressed as follows:

$$v = \frac{\zeta \cdot K \cdot H}{4 \pi \eta}$$

v is the velocity of cataphoresis, K the dielectric constant of the solvent medium, H the applied electrical field, i.e., the fall of potential within the solution, in

volt/cm., and η, the viscosity of the liquid. In this formula, all quantities except ζ, the potential difference of the double layer, can be measured experimentally, and so, from the data given by a cataphoresis experiment, ζ may be calculated. Such cataphoresis experiments are especially practicable in colloidal solutions in which microscopically or ultramicroscopically visible particles move with well measurable speed under the influence of an electrical field. In numerous experiments of Ellis, Powis, Svedberg and others the potential of the double layer in colloidal micellae were found to be about 20, 30, 40 millivolts in stable colloidal systems and 10 millivolts and below when there is no longer stability and flocculation of the micellae occurs, as *in the case of an easily flocculable colloid*, a hydrophobic colloid. Therefrom it might be concluded that firstly two groups of colloids exist; in the one of these stability is lost as soon as the potential has decreased to a certain critical point, as a rule about 7 to 10 millivolts; in the other group solubility still remains after the potential has disappeared. So, there is a close connection between the potential of the double layer and the stability of certain colloidal solutions, which requires an explanation. There are two explanations:

The one has been first advanced by Bredig, starting from the phenomena of surface tension of the mercury meniscus, which Lipmann found to depend on the difference of the potential of the mercury against

the solution. The surface tension has a maximum when the electrical charge of mercury is equal to zero, and falls whenever an electrical double layer is formed at the boundary, the sign of the charge being of no account. The reason is that the electrical elementary particles of equal sign situated within the surface counteract the mechanical surface tension, by electrical repulsion. Mechanical surface tension aims at contracting the surface, electrical charge of the surface aims at expanding the surface. Bredig transferred this theory to colloidal particles by assuming that the boundary tension of the colloidal particles against the solution should decrease with increasing electrical charge of the surface. Increasing of surface tension favors the tendency of the particles to reduce the surface by amalgamating or cohesion of several smaller particles so as to form one larger particle.

The other interpretation may be comprised thus. Let the two spherical particles which are surrounded by an electrical double layer be situated far distant from each other. They do not influence each other at all, as in a spherical condenser, the whole effect both of the positively and the negatively charged layers may be considered as being united in the center of the sphere, hence it follows that the total effect is 0. However, when, in consequence of molecular movements, two of such particles approach very near to each other, electrical repulsion between

the two envelopes just touching each other, and alteration of the distribution of electricity within the surface of the sphere occurs. The two particles then behave like particles of equal electrical charge and repulse one another. The particles do not behave like this originally, as they do not contain any *free* electrical charge at the surface like a piece of sealing wax when electrified, but they only contain an electrical *double layer*. Instead of which we may also say: repulsion of such particles does not increase according to Coulomb's rule, viz., inversely proportional to the square of the distance, but to a much higher power of this distance. It is as though the particles were surrounded by an elastic cushion, the repulsive effect of which does not appear before contact is made. When a colloidal solution is sufficiently dilute, there is practically no measurable repulsion among the particles suspended, even when strongly charged. Only because of this fact was Perrin able to calculate the Avogadro number from the distribution of the particles of a mastic suspension exposed to the action of gravity. He was able to consider the gravity as the only factor which determines the equilibrium of the local distribution of the particles in such a suspension, and to neglect any electrical repulsion which should occur between the particles. This repulsion becomes measurable only when two particles approach so closely as to almost touch one another, and then the effect of

it is to prevent the *complete* contact of the two particles. When, however, the potential of the double layer is sufficiently small and can no longer prevent the contact, which is aimed at by the molecular movement, the elastic effect disappears and adhesion of the two particles may occur, *provided the other conditions of a stable adhesion are given.* So this theory does not explain the essential cause of adhesion, but it does explain why particles fit for adhesion are prevented from so doing, by an electrical charge.

Thus, we have two explanations for the effect of the electrical double layer, and we may choose the one or the other. Properly speaking, I cannot see any essential difference between these two representations. Bredig's theory deals with *tensions* of surfaces: mechanical surface *tension* and electrical surface *expansion*, or, let us say negative tension. Forces like these are especially available for thermodynamic considerations. The other representation deals with molecular *adhesion* forces or *attraction* and electrical *repulsion* of ions of homonymous electrical charge. However the effect of mechanical surface tension is only a phenomenon to be reduced to molecular attraction or adhesion, and electrical surface expansion is a phenomenon to be reduced to electrical repulsion. The representation by means of attraction forces has the advantage of a greater amount of physical evidence. The other representa-

tion cannot be *wrong*, it is true, however, it is a little dangerous to conceive surface tension through an image which is not reduced to molecular attraction. So the Gibbs theory of adsorption, which deals only with surface *tension* has proved itself as practically rather fruitless and sometimes misleading, while the theory of Harkins and Langmuir, which is based on the theory of molecules and intermolecular attraction forces, manifested an utmost fertility which is by far not yet exhausted. We should, therefore, rather avail ourselves of the representation by means of molecular adhesion and electrical repulsion, than the one which deals with tensions. Unfortunately a really quantitative development of the theory is not possible yet in either direction.

In any event it may be understood that the electrokinetic phenomena have an intimate relation to the other electrical phenomena of colloidal solutions. By means of the theory of electrical double layers we can comprise two groups of phenomena in colloidal matters: cataphoresis, etc., and on the other hand, stability of colloidal solutions. Now, hitherto, we have considered these electrical phenomena only from a *physical* point of view; they become really available for colloid chemistry only by a consideration from the *chemical* standpoint. Hitherto only physical quantities were considered: *electrical density* of the double layer as a layer of two *surfaces;*

the *distance* of the two layers, and the difference of their *potential*. The material substrate to which these qualities are bound has not yet been looked for. The substrate of the electrical charges being the *ions*, the phenomena are evidently not sufficiently described by simply talking about positively or negatively charged elementary particles without regarding their chemical individuality. So we should try to describe the *chemical constitution* of the double layers, to regard the chemical nature of the ions which form the double layer. This question includes the investigation of the source of the ions of the double layer. We do not doubt that these ions of the double layer are present in the solution, too, and that the double layers only represent a peculiar *local distribution* of certain ions which would be present even if no double layers were formed.

III. THE ORIGIN OF THE ELECTRIC DOUBLE LAYERS

If we use the conception of adsorption in a sense as wide and merely formal as formerly given, we may assert without hesitation that the double layers fall under the *adsorption phenomena*, for there are some ions or others at the surface layer in another concentration than in the inside of the solution. But this suggestion is only a formal one, it does not satisfy us, and I shall attempt to discuss the different possibilities of producing a double layer at a surface, and to substitute the general and indefinite term of adsorption by several definite statements. I have attempted this in the past not such a long time ago, and I think I may still maintain those former suppositions, only I must add now some qualifying statements which may complete the theory, without however being able to exhaust the entire problem.

It seems to me there are three possibilities which might cause the formation of a double layer. I shall designate them provisionally, briefly as follows: (1) Double layers in consequence of appositional adsorption, (2) double layers in consequence of the tendency of dissociation in colloidal particles, (3) double layers produced without active chemical participation of the chemical material of the boundary surface. I shall begin with

A. DOUBLE LAYERS IN CONSEQUENCE OF APPOSITIONAL ADSORPTION

Lottermoser found the following fact: when a precipitate is produced by mixing a solution of silver nitrate and potassium iodide, the produced silver iodide is positively charged when an excess of silver nitrate is in the solution; it is negatively charged when there is an excess of potassium iodide. Both the positive and the negative charge of the particles prevent their sedimentation, and only in an intermediary zone, when the electrical charge has disappeared, a rapid sedimentation and coagulation of the silver iodide takes place. That may be easily observed when silver nitrate is titrated with potassium iodide; the endpoint of the titration becomes approximately manifest, even without an indicator, by the sudden coagulation of the silver iodide, which is kept in suspension before the endpoint has been reached, or if an excess of potassium iodide is added rapidly beyond the endpoint of the titration. The reason for this phenomenon may be easiest conceived according to an idea of Haber applied by him to adsorption generally, which, however, seems to hold only in certain cases of adsorption, and especially in this case of silver titration: the crystal grating of silver iodide is one of that cubical order known to you, in which each valence is dissipated in six directions. It must be realized that

those silver ions of the crystal which are situated in the surface of the crystal have a partial valence free and directed outward, and likewise the iodine ions on the surface of the crystals have a partial valence free. Whatever may be the modern interpretation of chemical valence and whatever explanation may be substituted for the one here used, at all events the theory of the crystal grate compels us to accept the idea that the surface of a crystal is unsaturated in respect to the atoms or ions within the crystal. Hence we may assume the superficial silver ions of the crystal to attract iodine ions from the solution, and the superficial iodine ions of the crystal to attract silver ions from the solution. Such an adsorption may be called *appositional adsorption.* According to the concentration of the silver ions and the iodine ions in the solution the crystal should be expected to adsorb either silver ions and to assume a positive charge, or to adsorb iodine ions and to assume a negative charge. The ion which is adsorbed at a higher rate determines the sign of the charge of the solid surface, while the ion inferior in rate of adsorption determines the sign of the other layer. The positive layer of the fixed silver ions brings about an accumulation of negative ions at a certain distance by electrostatic forces, or vice versa. This second ion layer is situated in the fluid part which is not adherent to the solid surface of the crystal. It need not necessarily represent a proper

surface in the mathematical sense, but the fact is better expressed by admitting the concentrations of the iodine ions of the solution to be larger in the neighborhood of the positively charged surface of the crystal than it is generally within the solution at any place sufficiently distant from this surface. This latter idea has been emphasized by Gouy, and we shall return to it several times later, for it is valuable for the conception of all kinds of double layers.

We shall now proceed to the second form of double layers, the

B. DOUBLE LAYERS IN CONSEQUENCE OF THE DISSOCIATION TENDENCY OF A COLLOID

Here also let us illustrate the point by an example. There are many chemical compounds which, according to their chemical constitution, may be called heteropolar and even rather strong electrolytes, *if they were soluble in water*. For instance resinic acids such as mastic; nucleic acids; silicic acid; the higher aliphatic acids and soaps. According to the investigations of McBain we may have the following image of a soap solution. The sodium salts of higher aliphatic acids are not dispersed to single molecules or ions but form micellae, the interior of which contains fatty acid and sodium. The soap solution, however, has a relatively high conductivity for the electric current, sodium ions

migrate toward the cathode, and micellae of fatty acid, which include sodium, migrate to the anode. We may assume that a micella consists of a nucleus of the sodium salt of a fatty acid, which cannot be considered as being in the state of real *solution* and does not dissociate into sodium ions and acid anions, at least it does not, in so far as these ions cannot be separated from each other by the electric current, because they form a solid micella. Only at the surface a dissociation of the salt takes place: an electrical double layer is formed. The exterior layer is formed by sodium ions, the interior layer by the ions of the fatty acid which, however, have no tendency to expand into the watery phase but stick at the surface of the micella. Thus the exterior layer is formed by numerous sodium ions, the interior layer is formed by a single ion of huge dimensions which contains numerous negative charges at the superficies. Let us also consider the conditions in a colloidal mastic solution. Mastic is evidently an acid according to its chemical behavior, but it is not soluble in water, only in alcohol. When an alcoholic solution of mastic is precipitated by adding water, the precipitate of the mastic acid forms very small micellae which do not coalesce but form a stable suspension in consequence of the protective effect of the double layer. This double layer may be imagined to be formed by the dissociation tendency of the micellae. The acid dissociates at least at

the superficies of the micella and forms hydrogen ions and acid anions. The acid anions have no tendency towards being dispersed to single ions but stick at the superficies of the micellae. We have, according to the suggestion of Harkins and Langmuir, to imagine these anions to be elongated molecules the negatively charged ends of which are directed towards the surface of the water, the other ends being fixed at the micella. The hydrogen ions on the contrary are free and aim to expand into the water, but in consequence of the electrical forces these hydrogen ions gather surrounding the micella, thus forming the exterior layer of the double layer. Just as in the case mentioned above, we need not suppose them to form a real surface but to be dispersed in a certain volumetric dimension. This "diffuseness" holds for all double layers, as Gouy emphasized. Therefore colloid acids, when suspended in pure water, as well as common acids, increase the quantity of the hydrogen ions, but they do not increase the concentration of the hydrogen ions at any place within the solution, they only bring about an accumulation of hydrogen ions round the micellae.

If such a colloidal acid is dissolved not in pure water but in an aqueous solution of electrolytes, according to the conditions an exchange of hydrogen ions and other metal ions may take place, and this process is analogous to the formation of a *salt* in common acids.

Such a tendency to superficial dissociation may be supposed to exist in many inorganic colloids, too, e.g., in colloidal ferric hydroxide. However, these cases are more complicated, because the chemical constitution of the superficies of the micellae in such sols are as yet very little known. Certainly the superficies of a micella of ferric hydroxide contain chlorine in some complex combination, and the double layer is probably formed by a mixture of ions. For this reason the theoretical considerations should be started from that much more simple case of a mastic solution. We shall try to do so.

We may call a colloidal substance which has the chemical characteristics of an acid, yet produces no discrete but only colloidal ions, an *acidoid*, in distinction from a truly soluble *acid*. When we bring such an acidoid into aqueous solutions of varied hydrogen ion concentration, avoiding the presence of ions as easily adsorbable as calcium or aluminum we may assume the exterior layer of the double layer to be formed only by hydrogen ions and the potential difference between the two layers to depend only on the hydrogen ion concentration. This phenomenon appears to be very similar to a metallic platinum-hydrogen electrode the potential of which also depends only on the hydrogen ion concentration. Many years ago I emphasized this analogy, comparing the micellae of colloidal acid to a hydrogen electrode. I then expressed the conjecture that

the potential of such an "electrode" might depend on the hydrogen ion concentration according to the same logarithmic law as that holding for the potential of a metallic electrode. This supposition has not been experimentally confirmed. According to this law, one should have expected that a variation of hydrogen ion concentration in the proportion of 1:10 should produce a variation in the potential of 58 millivolts. This variation is really much smaller, and, secondly, it is not constant for each power of 10 of hydrogen ion concentration. In figure 1 you see the reproduction of an experiment which I performed with Miss Domboviceanu, in which the potential of mastic particles is represented as a function of the pH of dilute acetate buffers. You see (fig. 1) that the change of potential of the mastic particles for a unit of pH varies between 4 and 11 millivolts, nowhere at any rate approaching 58 millivolts. The scale of the ordinate on the left-hand side shows the velocity of cataphoresis, the scale on the right hand side the potential calculated from the cataphoresis by means of the Helmholtz-Perrin formula. The left end of the curve is confined by the fact, that with increasing acidity flocculation occurs and the cataphoresis experiment is no longer possible. But we are allowed to complete the approximative course toward the left-hand side of this potential curve by the following considerations. We may be convinced that mastic cannot be charged *positively*

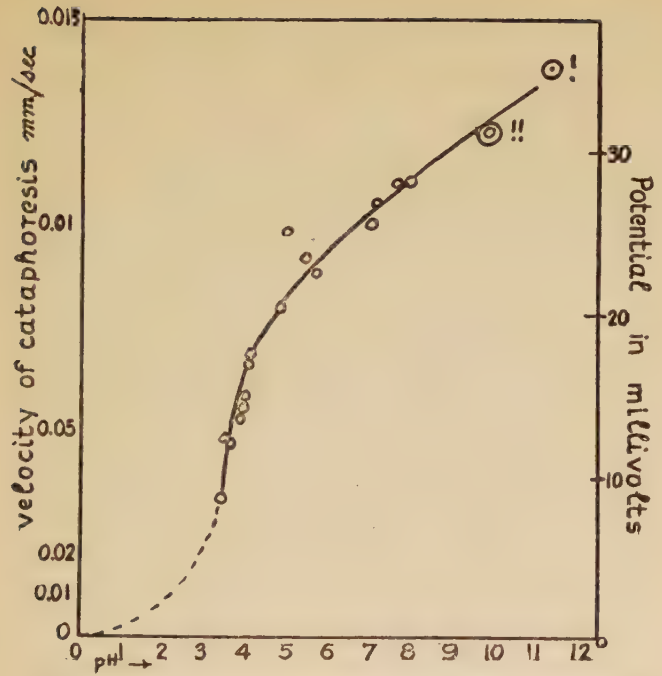

FIG. 1. Mastic sol in a feeble acetate buffer solution is exposed to an electric field. The abscissa is the pH, the ordinate, on the left-hand scale, gives the velocity of cataphoresis, calculated for the unity of the electric field (drop of the potential = 1 volt per cc.) in mm/sec. The right-hand scale of the ordinate shows the potential of the mastic particles against the solution as calculated from Helmholtz-Perrin's formula. The dotted part of the curve is an arbitrary extrapolation, experiments being impossible because of the flocculation in acid solutions. The experiments designated by ! have not been made with a real acetate buffer but with a feeble NaOH solution containing the same amount of sodium acetate as in the rest of the experiments (0.01 N). The experiment designated with !! has been made with a feeble solution of Na_2CO_3. (From a paper by Michaelis and Domboviceanu, 1923.)

by any ever so high an acid concentration. Therefore the left-hand end of the curve must have a course asymptotic towards the zero point of the potential, such as in the dotted part of curve, and the potential never passes below this zero line. That is in strict contradiction to the logarithmic law of Nernst in a metallic electrode. Well, I think the analogy to a hydrogen electrode was a fundamental mistake, the explanation of which seems to me very important for the further development of the theory. Therefore I wish to dwell somewhat on this subject.

In a metallic hydrogen electrode we may assume two quantities of opposite sign according to Nernst. The hydrogen gas has a tendency to emit *positively* charged hydrogen ions into the solution, the electrode then remaining *negatively* charged. On the other hand the hydrogen ions of the aqueous solution have a tendency to settle over the metallic surface, the metal then being *positively* charged. According to the hydrogen ion concentration the one tendency or the other prevails, and the electrode is sometimes positively charged and sometimes negatively. The absolute zero point of charge is given approximatively in a pH = 4.5, calculating from the well-known absolute potential of the calomel electrode. Thus, there is a definite pH in which the charge turns and which we might call the isoelectric point of the electrode.

In a colloidal acidoid the conditions are quite different. It is true, an acidoid has the tendency to emit hydrogen ions, too, and therefore to become negatively charged. But the hydrogen ions of the solution have *not* any tendency to settle over the surface of the solid particle so as to charge it positively. At most, a number of hydrogen ions corresponding to the superficially situated anions of the solid particle may fix themselves to the surface, the charge then being = 0. More hydrogen ions than these are not able to stay at the surface, and no positive charge of the surface can arise. At the best, discharge takes place, when the hydrogen ion concentration is very high. This is analogous to the case of a true weak acid the dissociation of which may be suppressed by the presence of a strong acid which produces a very high hydrogen ion concentration. But a *positive* charge of the anions of the weak acid can never be brought about by any strong acid in a concentration however high.

Now, mastic and other acidoids, though not being positively charged by *acids*, are sometimes positively charged by trivalent metal ions, such as those of aluminum. We shall return to this problem a little later.

However, there are also colloidal substances the charge of which is sometimes positive and sometimes negative, according to the hydrogen ion concentration, such as protein substances, e.g., casein, glob-

ulin, gelatin. They have an isoelectric point at a definite hydrogen ion concentration characteristic for each protein. In this case, the similarity to a metallic electrode is more evident, and the reason is that colloids really have the tendency both to emit and to fix, or "adsorb," hydrogen ions since they contain both carboxyl and amino groups. The carboxyl group emits a hydrogen ion, the amino group combines with a hydrogen ion according to the scheme:

(1) $NH_2 \cdot R \cdot COOH \rightarrow NH_2 R \cdot COO^- + H^+$

(2) $COOH \cdot R\,NH_2 + H^+ \rightarrow COOH \cdot R\,NH_3^+$

The formula (2) means the same as the more usual form of writing:

(2a) $COOH \cdot R \cdot NH_2 + H_2O \rightarrow COOH \cdot R \cdot NH_3\,OH \rightarrow COOH \cdot R\,NH_3^+ + OH^-$

But since the molecule $COOH \cdot R \cdot NH_3OH$ has a somewhat problematic meaning and in any event can only be present in an extremely low concentration, one should prefer the formula (2). Now you see, in the reaction (1), the protein *loses* hydrogen ion, in the reaction (2), the protein "adsorbs" a hydrogen ion. This kind of colloid, on the one hand is more analogous to a metallic electrode, since there is an isoelectric point; on the other hand, the *chemical* analogy is directed toward an amphoteric soluble electrolyte such as an amino acid, and we may call

these colloids *ampholytoids*. As the simple fatty acids, with the increase of the molecular weight, form a gradual transition to the colloidal acidoids, so the simple ampholytes gradually turn into colloidal ampholytoids by increase of the molecular weight or other conditions which augment the colloidal properties.

If we compare the double layers in consequence of an appositional adsorption with those in consequence of dissociation tendency we see that the difference is not very considerable. In either case we have a dissociation tendency. For, instead of saying: the superficies of solid silver iodide adsorb silver ions, we may also say, these superficies lose iodine ions because of a dissociation tendency. The difference is only, that in a case, such as mastic, the negative ions of this acid can never be emitted into the solution on account of their colloidal behavior, while in the case of silver iodide either ion, which is produced by the dissociation tendency, may be the one emitted into the solution. After all, in both of these cases the ions responsible for the charge of the double layer, are formed from an electrolyte-like substance for the same reason as the ions of a common electrolyte are formed by the undissociated electrolyte.

We have not yet exhausted this kind of double layer and shall return once more to them, especially in connection with the question of the reversibility

of the sign of the charge. But first let us proceed to the third group of double layers.

C. THE DOUBLE LAYERS FORMED WITHOUT ANY ACTIVE PARTICIPATION OF THE COLLOIDAL PHASE

Neither of the possibilities just discussed is sufficient to explain all double layers that may occur; they only suffice in the case of such colloids the micellae of which consist of a heteropolar electrolyte-like chemical compound. However, experience has taught that at the boundary surfaces of materials chemically wholly indifferent and not dissociated at all, generally an electrical double layer is also formed. To give some examples, the surfaces of cellulose, paper, parchment paper, collodion, even gas bubbles, are mostly negatively charged against aqueous and even sometimes non-aqueous solutions. It is striking that the aqueous phase is almost throughout negatively charged. Coehn pointed out a rule according to which each phase with a higher dielectric constant is negatively charged in respect to another phase with a lower dielectric constant. Quite generally this rule is certainly not fully adequate, for in this case there could not exist any substance positively charged against water which has such a high dielectric constant; yet there are plenty of such. This rule becomes a little more suitable, when restricted to substances not tending to the

formation of ions. However even then we had better to restrict the consideration to systems containing water, since we are too little informed about the charges of surfaces of phases not containing any water. And so we may confine ourselves to the following assertion: any substance of electrochemically indifferent character is negatively charged against aqueous solutions or against phases containing water. Positive charges occur extremely seldom in such cases, even under such conditions where electrolyte-like phases of generally negative charge change the sign of the charge.

This is the best opportunity to return once more to the general problem of change of the sign of charge.

In the case of appositional adsorption in silver halides the conditions which may change the sign of the charge are quite evident. There must be a definite concentration of the iodine ions in the solution (or of silver ions, which depend on the concentration of the iodine ions according to the solubility product which represents the isoelectric point of the solid silver iodide. In fact, Fajans was able to determine this point.)

For the case of dissociation tendency of acidoids I first wish to recall the fact that all these acidoids do not change the sign of the charge by means of hydrogen ion concentrations however high. But when trivalent or quadrivalent metal ions are present they do change the sign of charge. For in-

stance, glass, silicates such as kaolin, furthermore, mastic, acquire a positive charge from aluminum salts in the lowest concentration. In opposition to this I wish to draw your attention especially to the fact that electro-indifferent substances such as cellulose, collodion, agar, do not even change their charge through aluminum salts. Very small positive charges in presence of aluminum salts have been described by Jacques Loeb. However, a charge of 3 to 4 millivolts calculated from cataphoresis experiments is perhaps within the limits of error of the method. We are only allowed to assert that the charge is diminished to zero. That has been found in my laboratory to hold true for cellulose, agar, collodion. J. Loeb pointed it out for collodion; but he added the important observation, that the *quadrivalent* thorium ion brought about a *positive* charge, in distinction to all of the uni-, bi- and trivalent ions.

The rule that a substance like collodion cannot be positively charged by a high hydrogen ion concentration holds only when protein substances are not present in the solution. Collodion adsorbs such substances, and then the superficies of collodion no longer behave like collodion but like protein, of course. Common amino-acids which are not adsorbed by collodion do not influence the original behavior of collodion. Neglecting this peculiar

se, viz., the covering of the superficies by a wash-

proof protein layer, the rule remains that collodion and such like electro-indifferent substances are always negative against any aqueous solution, except in the presence of the quadrivalent thorium.

Now we want to explain how a double layer of ions may be formed at the surface of quite indifferent substances, such as collodion and even air bubbles. A purely formal explanation is as follows: indifferent substances adsorb negative ions better than positive ions. I need not emphasize once more that adsorption has only a formal meaning and does not involve the supposition that the adsorbents actively participate in adsorption: it is an *apparent* adsorption. The real cause of this phenomenon is somewhat problematic. The fact that, quite generally, even without a reasonable chemical cause being given, any boundary surface seems to have an electrical double layer and that only in special cases the potential of it can be = 0, leads us to the following suggestion. In a solution of electrolytes, there is a mixture of equal amounts of positive and negative ions, and the electrical effect towards the surroundings is compensated only if the average distribution is regulated by the laws of probability, and any special causes of distribution contradictory to the maximum probability are lacking. Now, at the superficies of a solution, of electrolytes as well as of non-electrolytes, there may be special conditions, which, in the case of non-

electrolytes, are known as surface tension, capillary activity, etc. It would be a useful hypothesis to attribute a definite capillary activity to each single kind of ion. Such an assumption would be a suitable paraphrase of the fact that the ions of the superficies in an electrolyte solution tend to assume a peculiar order so as to form a double layer even without exterior forces being active. The more capillary active ions form the exterior layer, the less capillary active ions form the interior layer. In order to explain the negative charge of the exterior layer, which is to be found electronegative as a rule, we had to attribute a higher capillary activity to the negative ion, generally, than to the positive ions. It may be reserved to the atomic physicist to explain this behavior, which we must necessarily assume in order to conceive the electrical double layers.

I proposed some years ago the following working hypothesis. Suppose hydroxyl ions are more capillary active than hydrogen ions, any surface of pure water must be negatively charged against the interior of the water, provided the superficies of the water touches a body with no forces directed towards the water which might disturb the distribution of ions. Jacques Loeb pointed out a similar idea: as we have been taught by Harkins and by Langmuir that molecules are often arranged in a definite direction when situated within the superficial

layer of a liquid, one might suppose the superficial molecules of water to be directed with the hydroxyl groups outward and the hydrogen inward. Recently Loeb has investigated the influence on this potential of the added electrolytes. He used such indifferent substances as collodion, graphite, gold sol, and estimated the potential from cataphoresis experiments. The negative potential was manifest even in pure water, but to a very small degree, scarcely exceeding about 7 millivolts. It increases by addition of any electrolytes and passes a maximum with increasing concentration, scarcely exceeding 60 millivolts. When the anions of the electrolyte are varied the negativating effect *increases* with the valence; when the cations are varied, this negativating effect *decreases* with their valence. The concentration of any electrolyte increasing, the potential generally finally becomes = 0. The trivalent ion of lanthanum in highest concentrations may perhaps cause a slight positive charge, which, however, in my opinion, certainly does not exceed the limits of error. Only the quadrivalent thorium, even in the lowest concentration, effects a strongly positive charge. This peculiarity of thorium ions has been likewise pointed out for the charge of air bubbles surfaces against aqueous solutions by McTaggart.

A few years ago I derived a rule from my investigations that changing of the sign of charge by polyvalent ions might be characteristic of acidoids, while

electro-indifferent substances keep the negative charge even in presence of polyvalent ions. I did not know then of the effect of thorium. We have to modify slightly this rule suggested by me, and we may summarize the theory of the change of sign of the charge in the following manner:

1. Particles capable of a *dissociation tendency* of an *amphoteric* character (such as proteins) can change the sign of the charge according to the *hydrogen ion* concentration of the solution, and at a certain pH there is an isoelectric point. The sign of the charge is also changed by polyvalent ions. Or in other words: the hydrogen ion concentration just sufficient to reverse the sign of the charge is diminished in the presence of other cations, and especially of polyvalent metal ions.

2. The sign of charge of particles which are considered as acids according to their chemical constitution, "acidoids," is not reversed by hydrogen ions in however high concentration; yet the reversal is effected by *trivalent* cations. (It does not seem to me to be certain that *bivalent* cations are able to do so; though the *discharging* effect of bivalent cations is evident to be much higher than the one of univalent metal ions, as a rule.)

3. Particles of quite indifferent nature, such as air bubbles, collodion, certainly do not have the sign of their originally negative charge changed by means of hydrogen ions in however high concentration, nor

do they so by other univalent or bivalent cations, nor do they almost certainly do so, even by means of trivalent cations either. Only the quadrivalent thorium ion reverses the charge, as far as we know.

Let us summarize the main contents of the considerations of the theory of electrical double layers: We may discriminate three kinds of double layers according to the cause which produces the separation of positive and the negative layer:

1. Double layers in consequence of an appositional adsorption of ions; illustrated by the example of silver iodide.

2. Double layers in consequence of a dissociation tendency of colloidal particles which, though not dissolved in water, yet behave like a soluble electrode in so far as to have the tendency to emit ions; illustrated by the example of mastic or soap.

3. Double layers in consequence of a different capillary activity of different ions; these occur at the boundary surface of such particles which are indifferent with regard to electrochemical affinities; illustrated by the example of air bubbles, collodion, agar.

Now, we should expect that the different tendencies of the different kinds of ions to accumulate in the superficies should be manifest in all cases, and not only when the solid particles are formed by a chemically indifferent substance. However, in those other cases, with chemical affinities predominating, the

effect of the spontaneous distribution of ions is generally far less than the other forces of a more chemical nature. In such cases when the adsorbent possesses a doubtlessly strong dissociation tendency, such as colloidal protein particles, the formation of the double layer is certainly regulated practically entirely by the dissociation tendency. In other cases, such as mastic sol, it has not yet been established whether or not besides the dissociation tendency the spontaneous distribution tendency participates in determining the properties of the double layer.

IV. THE PROPERTIES OF CHARCOAL

I do not doubt that this system of double layers is neither complete nor absolutely exact. However, no acceptable theory of double layers being available till now, it seems to be better to start from certain reasonable explanations and to attempt to improve them gradually rather than renouncing any theory. That being the case, we will not be surprised by facing cases which cannot be fitted easily into this system. We have to consider a special case of this kind now. If you will do so, you may consider this case as a quite peculiar one of appositional adsorption. This case is represented, for the inanimate world, by one single substance, charcoal. In living matter this case seems to occur very generally, for all respiring cell superficies are likely to behave in a similar manner. As is generally known, charcoal prepared from blood, wood, etc., has long been applied as an expedient adsorbing agent for dyestuffs and for purifying liquids. From the beginning of the investigations on adsorption most experiments have been made with charcoal because charcoal adsorbs better than any other powdered substance. Charcoal was considered as the prototype of an adsorbent, all other adsorbent materials being thought to differ from charcoal only quanti-

tatively. Its very great capacity of adsorption was attributed to the presence of an enormous system of superficies, not only in consequence of the finely granulated consistence but also because of the considerable unevenness or roughness of the particles and cavities of the superficies or, as it is usually called, the development of *interior superficies*. But the particular qualities of charcoal do not depend on the largeness of the specific superficies alone. This idea is entirely wrong and has brought about several distorted views. The adsorption faculty of a good charcoal is not only quantitatively but also qualitatively wholly different from any other adsorbing substance. There are only very few substances endowed with similar qualities and even that only in quite a small degree. Firstly: in distinction from most powderlike, however finely granulated substances, charcoal possesses a prominent faculty of adsorbing from aqueous solutions numerous non-ionized, electro-indifferent substances. Here the rule generally holds that substances are the better adsorbed the more they diminish the surface tension against air, in aqueous solution. As this capillary activity, according to a rule of J. Traube, increases rapidly with the length of the carbon chain, also the adsorbability by charcoal increases rapidly with the length of the carbon chain, according to a rule of Freundlich. However, this parallelism is not always evident when comparing

substances belonging to different homologous series. Not even does the rule hold that only such substances are adsorbed which decrease the surface tension against air. For instance, sugar is adsorbed by charcoal in a measurable quantity, though it increases the surface tension against air. Experience has shown that *any* substance dissolved in an excess of water is adsorbed by charcoal, and a so-called negative adsorption never occurs in dilute solutions, in contradiction to some earlier assertions, and this holds for electrolytes, too. There are only two substances known hitherto which are not at all adsorbed by charcoal: the sulfates of alkali metal ions, according to the investigations of Rona and myself, and glycocoll, according to Abderhalden and Fodor. Different kinds of charcoal are different in respect to their adsorptive capacity, but I formerly thought the special capacity in adsorbing capillary active non-electrolytes to be characteristic for all kinds of charcoal, though they may differ in other respects. But I have newly encountered a kind of charcoal prepared from pure gelatin which lacks even this faculty, e.g., of adsorbing octyl alcohol. Charcoal, even if it is ash free, is not necessarily elementary carbon, and the concomitant materials which may not quite justly be called *impurities*, determine to a great extent the physical properties. Many contradictions in the literature may be explained by the different method of preparing the charcoal. E.g.,

Perrin found by means of endosmosis experiments charcoal to be electronegative in alkaline solution and electropositive in acid solution. Bethe and Toropoff found cylinder charcoal to be negative under any condition. In my laboratory Gyemant and later Umetsu confirmed Perrin's statement when using blood charcoal, while the latter in a charcoal prepared from sugar verified the result of Bethe. Rona and I pointed out that blood charcoal adsorbs basic and acid organic dyestuffs approximately at the same rate, in distinction from sugar charcoal, which, according to Umetsu, only adsorbs basic dyes and even these to a much lesser extent than blood charcoal.

Recently E. J. Miller found a completely pure charcoal, when treated by strong heating, to be activated for adsorption in a high degree and then to behave quite differently from those kinds of charcoal used in my experiments. This activated charcoal seems to me to be the most interesting kind because of its chemical purity, it being the only charcoal preparation consisting of pure carbon. For instance, this charcoal absorbs, from neutral salts, the acid component at a higher rate than it adsorbs the basic component, a hydrolysis taking place.

O. Warburg made a peculiarly interesting observation when using charcoal as a model for respiration experiments. As he pointed out, the oxidation of amino-acids is accelerated by charcoal,

and this catalytic faculty is in some way or other connected with the adsorption faculty, and I do not think that any other substance, however finely granulated, could be found suitable as a respiration model but charcoal. The oxidizing faculty of *blood charcoal* is poisoned by hydrocyanic acid, while the oxidizing faculty of *sugar charcoal* is not influenced by cyanides. As Warburg showed, this difference depends on the iron content of the charcoals: blood charcoal contains iron, sugar charcoal does not. This iron is present in a wholly unknown form, added iron salts can not replace the original iron content. Recently Warburg reported that small amount of hematin added to the sugar when carbonizing it, may impart to the sugar charcoal the quality of blood charcoal.

For our considerations of adsorption the great capacity of charcoal of adsorbing capillary active substances such as esters or octyl alcohol, is most important. Though there are some kinds of charcoal which lack this faculty—as mentioned above, yet it has to be appreciated, on the other hand, that in most of all other substances besides charcoal there is not even the smallest trace of an adsorbing faculty for any capillary active non-electrolytes.

However, this behavior towards non-electrolytes has no direct relation to our subject, as electrical double layers are not produced when non-electrolytes are adsorbed. It is only to prove that charcoal is

quite a peculiar adsorbent that I mentioned these points. This peculiarity will become evident also in regard to the behavior of charcoal towards electrolytes, to which topic we shall now proceed. For charcoal will also adsorb any electrolyte. Before taking up this point in detail I wish to discuss a phenomenon still obscure, the elucidation of which may be of great importance for the interpretation of the adsorbing property. That is the behavior of charcoal when exposed to a *mixture* of adsorbable substances.

When charcoal is in contact with a mixture of *two capillary active substances*, adsorption is determined by a rule pointed out 11 years ago almost at the same time by Freundlich and Losev, and by Rona and myself. The one substance partly displaces the other from the superficies and a feebly adsorbable substance can be almost completely displaced by a strongly adsorbable one. This rule has become of certain value in O. Warburg's researches on respiration both in living cells and in charcoal. He pointed out that all capillary active substances to be strongly poisonous for respiration, the effect increasing with the degree of capillary activity. The interpretation is easy. Well adsorbable but not combustible capillary active substances replace those substances which are oxidized by respiration on the surface, these substances being well combustible but less adsorbable than the poison.

H. Lachs and I pointed out this rule of substitution or replacement to hold only in a mixture of two capillary active non-electrolytes or two electrolytes (or better: in a mixture of two salts with a common ion the concentration of which is kept constant). But the rule of substitution does not hold when mixing a substance of the one kind (i.e., capillary active non-electrolyte) with a substance of the other kind (i.e., ions). In this case the adsorption of either substance is independent on each other, no replacement taking place. All exceptions to this rule are very small and partly of a doubtful nature. One might perhaps imagine the surface of charcoal to be like a mosaic composed of two different surface elements one of which adsorbs the one group, the other adsorbs the other group. It is a remarkable coincidence that Warburg also, in a quite different way, suggested the hypothesis of a mosaic structure of the charcoal superficies, places containing iron and places not containing iron. However, I emphasize that this only holds for blood charcoal and is not a general property of charcoal or elementary amorphous carbon.

After having claimed a quite peculiar position for charcoal within the group of adsorbing substances we proceed now to the behavior of charcoal towards electrolytes. I do not intend to exhaust this question but only to present some facts available for the theory of double layers. Here also most experi-

ments refer to blood charcoal and represent only a preliminary stage of investigation. However there is some experimental evidence available to show the essential differences of different charcoals. We observe directly only the adsorption of a complete electrolyte, not of a single kind of ion; but comparing the adsorption of different electrolytes with a common ion, the specific differences of the single ions may be learned at least relatively. From Rona's and my experiments the following series of adsorbability of different cations may be demonstrated.

$$\left.\begin{matrix} Na^+ \\ K^+ \\ NH_4^+ \end{matrix}\right\}; Ca^{++}; Mg^{++}; Al^{+++}; Cu^+; H^+; \begin{cases} \text{Alkaloids} \\ \text{and basic} \\ \text{organic dyes} \end{cases}$$

And as for anions, the following series was pointed out:

$$SO_4^{--}, Cl^-, Br^-, I^-, SCN^-, OH^-, \begin{cases} \text{Organic dyes;} \\ \text{Sulfosalicylic acid and some} \\ \text{other aromatic acids} \end{cases}$$

In the following table you may see some data on the adsorption of different electrolytes.

	$\frac{1}{2}SO_4^{--}$	Cl^-	CNS^-	OH^-
Na^+	0	6	29	39
K^+	0	6		
NH_4^+	0	7	36	
$\frac{1}{2}Ca^{++}$		13	55	
$\frac{1}{2}Mg^{++}$	6	14		
$\frac{1}{2}Zn^{++}$		21		
$\frac{1}{3}Al^{+++}$		27	63	
$\frac{1}{2}Cu^{++}$		38		
H^+	47	59		

In the left vertical column is given the cation, in the horizontal line the anion of each electrolyte studied. In all experiments 100 cc. of a 1 N solution of the salt were shaken with 15 grams of blood charcoal, the figures represent the percentage of the adsorption of the salt. From this table you may see the way in which the series of ions shown before were obtained. As for cations, the adsorbability is rather parallel to the valency, only the hydrogen ion is exceptionally strongly adsorbed, even more than trivalent ions. Among the univalent alkali ions no difference is to be seen; what we call the "Hofmeister series" does not hold here. However in anions, the valency is less important and the Hofmeister series becomes evident, which, however, is to be the subject of the next lecture. Hydroxyl ions are extremely strongly adsorbed. Hydrogen- and hydroxyl ions are surpassed in adsorbability only by some organic ions, such as dyestuffs, alkaloids and, as a very interesting example, by sulfosalicylic acid, which is a very strong electrolyte, and may be considered as completely dissociated in aqueous solution. This acid is very suitable for adsorption analysis of ions, because the rôle of non-ionized molecules can be neglected, as it can in the so-called strong inorganic electrolytes which were the subject of investigation represented by the table given above.

All of these facts concern blood charcoal. As for sugar charcoal, the following at least may be

pointed out. Sugar charcoal is not so much inferior in adsorbing capillary active substance—at least it need not be much inferior—but it is much inferior in adsorbing electrolytes. The anions of acid dyestuffs—as far as they form true aqueous solutions—are not adsorbed at all, and we may conclude from this that the simple inorganic anions are certainly not adsorbed. On the contrary, basic dyes such as methylene-blue are adsorbed by sugar charcoal at a clearly remarkable rate.

As you see, charcoal is the most suitable and most accessible substance for chemical analysis in adsorption work. For that reason it is the best object also for controlling the theory of electrical double layers. In cataphoresis experiments with charcoal we can recognize the sign of the charge; when we perform a cataphoresis experiment with charcoal in different electrolyte solutions, we know which ion of the electrolyte applied is better adsorbed and thus we can anticipate the sign of the charge and confirm it by the cataphoresis experiment. The direct adsorption experiments, it is true, do not give us *absolute* values for the adsorbability of the single ions. If we employ, however, an electrolyte such as HCl, we may assert from our investigation, that H^+ is better absorbed than Cl^-, etc. In the case of KCl, we cannot directly decide whether K^+ or Cl^- is better absorbed, since the analytical data do not allow us to compare the adsorbability of a cation and

of an anion, but only the adsorbability of two anions, or of two cations. However, since we see that H^+ is placed almost at the end of the cation series and Cl^- is placed at the beginning of the anion series, H^+ may be considered as more adsorbable than Cl^-. Through such kind of consideration we can, at least in some cases, anticipate which ion of an electrolyte will be better adsorbed. Provided our representation of the origin of the electrical double layers is justified, we are able to anticipate the sign of the charge of blood charcoal when it is in contact with electrolyte solutions: that ion which is more strongly adsorbed will determine the sign of charge of the charcoal, the other ion determining the sign of charge of the solution.

Let us predict the results to be expected in certain cases. Since blood charcoal adsorbs both hydrochloric acid and sodium hydroxide, and since charcoal adsorbs hydrogen ions better than most of all other cations, and hydroxyl ions better than most of all other anions, the charge of charcoal should be expected to be positive in hydrochloric acid and negative in sodium hydroxide, an isoelectric point being at a reaction perhaps approximately neutral. Since in sulfosalicylic acid the anion is an extremely well adsorbable one, charcoal should be expected to be always negative in presence of sulfosalicylic acid. Since sugar charcoal does not adsorb any acid, a change of sign of that negative charge which may be

expected in electro-indifferent substances, should not be expected even under the influence of strong acids. *In fact all these expectations have been confirmed by the cataphoresis experiments* quoted above, especially by Gyemant and Umetsu in my laboratory.

The present stage of knowledge about adsorption and cataphoresis is still insufficient, the conclusions reached from experiments have a preliminary character, but these considerations may have convinced you of how important this subject is for a general theory of electrical phenomena. They are especially important for biologists, for many observations seem to hint that the surface of the living cells need not be analogous to common superficies such as the one of silicates or mastic or ferric hydroxide, but just to charcoal. There is one fact which directly leads us to such a conclusion. I told you before that scarcely any substance can be found which adsorbs capillary active non-electrolytes except charcoal. Now, O. Warburg has proved animal cells, such as red blood corpuscles, to adsorb capillary active substances, even though the cells have been carefully extracted free of all lipoid substances, which perhaps might absorb the capillary active substances by a simple solution process. For all capillary active substances are easily soluble in lipoids. However, the cells appear to possess a real adsorbing faculty for capillary active substances, and that holds in

the inanimate models only in charcoal. Warburg himself formerly assumed this faculty to be a common property of any superficies, but I have shown you that is not the case. Charcoal is not a model for *any* superficies, but just a model for those superficies which have the important function for *respiration in living cells.*

V. THE CONNECTION BETWEEN DISCHARGE, ADSORPTION, AND FLOCCULATION

The most important reason for discussing the electrical double layers formed at the superficies of suspended particles is the connection of this electrical charge with the condition of a colloidal system. The leading idea for a biologist is that the condition of the colloidal material of the living cells, either the colloidal *contents* of the cell or the colloidal *membrane* of the cell, rule the vital function of the cell, such as respiration, permeability, irritability, etc. Now, the condition of the colloidal material depends on the electrical charge of the micellae, and so we recognize a connection between the vital function of the cell colloids and the electrical charge of their micellae. That is the reason why we are interested in the relation between the electrical charge and the colloidal conditions, in a colloidal solution this problem being the necessary preparation for the physiological problem just mentioned.

The changes of colloidal conditions in living cells within the physiological limits are *reversible* and relatively of a *small extent.* They are necessarily *reversible,* because an irreversible change, e.g., an irreversible flocculation of the protoplasm, is not

compatible with life and means death of the cell. They are of relatively *small extent* in so far as evidently very small changes of the colloidal structure may be followed by great physiological reactions. In opposition to this, we have to begin by studying the *great* alterations in colloidal conditions in our preliminary work on artificial and simple colloidal system. The most evident alteration of the conditions in a colloidal solution is the *flocculation* produced in a solution which was stable before. This phenomenon is the one easiest to be observed and most evident. Generally such a flocculation is brought about by adding electrolytes. On the other hand, we recognize a connection between flocculation and discharge. So we should suppose that the flocculating effect of electrolytes depends on a discharging effect, and so the important problem arises: *Why do electrolytes added to a colloidal solution influence the electrical charge of the colloidal micellae?* Now experience has taught that very often the added electrolyte is adsorbed by the colloidal particle, and so, we might suppose that the *adsorption* of an electrolyte has some connection with its *discharging faculty*. So let us begin the discussion of the influence of electrolytes on the flocculation by the consideration of the *connection between flocculation and adsorption of the flocculating electrolyte.* Again, we might elucidate the point by

an example in the light of an investigation on mastic sol which I carried out many years ago.

When a mastic sol is flocculated by an electrolyte this electrolyte is always found to be partially adsorbed by the flocculated particles, except in two cases. These exceptions are: flocculation by acids, and flocculation by the neutral salts of alkali metals. This second case, however, must be considered as doubtful, for the following reasons. Trivalent cations flocculate in a very low concentration, and adsorption then occurs at a considerable rate, as can be easily demonstrated by chemical analysis. Bivalent cations bring about flocculation only in higher concentration. The *absolute* amount of the adsorbed cations is probably approximately the same as in the case of trivalent cations. But the *relative* amount being much lower, the adsorption cannot so easily be shown by chemical analysis. For this chemical analysis consists of the comparison of the concentration of these ions, calculated from the known amount added and the amount found in the filtrate. If this *concentration* is high, a relatively large *absolute* amount of the ions may have disappeared by adsorption without lowering the *concentration* in a measurable degree. But after all, we are just able to prove the adsorption for bivalent cations. In univalent cations the concentration sufficient for flocculation is still much higher. Though these might be adsorbed at the same *absolute* rate

as polyvalent cations, this amount is no longer demonstrable by chemical analysis. Therefore, the fact that in univalent cations adsorption is not manifested by chemical analysis, is likely to be only the consequence of a technical insufficiency. In opposition to this, in the case of flocculation by *acids*, such an interpretation would not satisfy us at all. I wish to emphasize this fact on account of its great theoretical importance. A mastic solution is flocculated by an extremely dilute solution of hydrochloric acid, about 10^{-3} to 10^{-4} N. The conditions for analyzing chemically the deficiency of the acid, which might be connected with the flocculation, are most favourable. If there would be any adsorption of the acid we should be able to prove this adsorption very easily. However, acids bring about flocculation without being adsorbed at all. The most likely interpretation of this fact can be easily derived from the theory of the origin of the electrical double layers in mastic sol presented in my first lecture. The effect of the acids consists of a counteraction by the hydrogen ions of the acid against the tendency of the mastic particles to emit hydrogen ions into the solution. The hydrogen ions of the solution suppress the dissociation tendency of the mastic and so discharge the electric double layer. The single micella of a mastic particle may be considered as an electrical spherical condenser. The interior electrical layer is the superficial but

adherent layer of the colloidal ions, the exterior layers is the couch of hydrogen ions. According to Gouy, these hydrogen ions do not form a real surface layer in the mathematical meaning of "surface," but in consequence of the diffusion tendency of the hydrogen ions towards the solution there is a stationary fall of the hydrogen ion concentration from the micella toward the solution. In considering the entire particle as an electrical condenser and calculating its potential, we may substitute for this "diffuse" layer of hydrogen ions a real positively charged *surface* at a *definite distance* from the negatively charged surface in such a manner that the entire electrical charge of the hydrogen ion layer is united in a surface, which represents the centre of gravity of the electrical charges. In this manner we may define the concept of a definite *distance* of the double layer on which the potential difference of the condenser depends. The hydrogen ions of the aqueous solution exert a counterpressure against the diffusion tendency of the hydrogen ions of the double layer. The higher the hydrogen ion concentration of the solution, the smaller is the "distance" of the two layers of the condenser, and furthermore, the smaller is the potential difference of the condenser. This potential difference being diminished to the "critical" value, flocculation occurs. *In the flocculating effect of acids, the effect of diminishing the*

potential difference may be immediately understood without any adsorption interfering.

However, in all of the other cases, there is an evident connection between adsorption and discharge. As for the kind of adsorption, as a rule, we are compelled to accept that kind of adsorption which I called adsorption "by exchange" or "by substitution." E.g., when a negative sol is suspended in a solution containing only univalent cations in a low concentration, and it is flocculated by adding a small amount of bivalent ions such as calcium, then this calcium is found to be partially adsorbed by the precipitate. Here we may assume that calcium has taken the place of an univalent ion which originally formed the exterior layer of the double layer. Adsorption then means a substitution. Thus our problem is reduced to the following question: why is the potential of the double layer smaller after some univalent ions have been substituted by calcium?

The difficulty of this question is that the exterior layer consists no longer of a single kind of ions but of a mixture of ions. For when increasing amounts of calcium are gradually added to the sol, a *gradual* substitution of the original hydrogen ions by calcium ions will occur, and not before a marked excess of calcium has been added, will the substitution be practically complete. There is no reason to assume the substitution to be complete in that concentration of calcium chloride which is just sufficient to

bring about the flocculation. At first, a specific coagulating effect of calcium might seem to exist, but this assumption is wrong. For, when we add to an aqueous mastic sol hydrochloric acid instead of calcium chloride flocculation occurs still more readily; we need much less hydrochloric acid than calcium chloride for a complete flocculation.

The connection between the substitution of hydrogen ions by calcium ions and the discharge of the particles may be interpreted by the following considerations. The original hydrogen ion layer of the colloidal particles is not a real surface, but it can be considered as being equivalent to a real surface, which contains all of the hydrogen ions of the colloidal acids, at a definite distance from the surface of the particles. However, instead of a *surface* we may imagine also a very thin *layer*, the hydrogen ion *concentration* of which has a definite average value. The difference between the osmotic pressure of all hydrogen ions within this very thin layer and of the hydrogen ions of the solution generally determines the osmotic counter-pressure which suppresses the dissociation tendency of the colloidal acid. Now, if some of the hydrogen ions of the double layers are replaced by calcium ions, the diffusion pressure of these layers toward the solution is diminished, or the osmotic counterpressure of the hydrogen ions of the solution is relatively increased. The distance of the double layers is diminished, and so is their potential difference.

Thus the discharging power of the calcium ions depends on their faculty to substitute the hydrogen ions of the double layer. Now, replacement of one ion by another ion means that the second ion is more easily adsorbed by a surface than the other ion is. Again the problem of the specific surface activity or adsorbability of the different ions arises which we cannot yet explain in a satisfactory manner. However, in all events, it has become clear that the discharging faculty of an ion must parallel its adsorbability. We have to put up with this qualitative information. All attempts to get clear mathematical conceptions have failed hitherto. Gouy has developed a theory of electrical double layers in a very exact and splendid manner. However, his considerations hold only under very simple conditions, viz., that first, the boundary surface of the two phases is to be a plane surface, not a sphere, and second, all effects of adsorption are to be neglected. Neither of these conditions can be dispensed with in real colloidal solutions. All attempts to adapt the simple theory of Gouy to the real conditions of colloidal solutions and to settle mathematical connections between the different magnitudes which might be confirmed by experiments met with considerable difficulties. It seems that in order to arrive at a satisfactory solution of this problem one should start from quite new fundamental suppositions. In the meantime we have to put up with the qualitative considerations given above.

VI. THE SO-CALLED DONNAN EQUILIBRIUM

Hitherto we derived all theories of the electrifying effect of ions from the concept of adsorption. Once more I emphasize that this concept has a purely formal meaning. It was only a fulcrum for a systematic treatise. So we should not be surprised that the electrifying effect of ions may be considered from quite a different point of view, and without contradiction. Now, indeed, recently a different theory has been developed which reduces the electrifying effect of ions on colloids to the so-called Donnan equilibrium. I shall first explain this theory in a few words and then discuss the problem of reconciling this theory with the other theories.

Twelve years ago Donnan developed the following theory. When a membrane separates two electrolyte solutions one of which contains an ion unable to diffuse across this membrane, the consequence is that the diffusible ions also tend to establish a condition of equilibrium which is anomalous compared to usual conditions. Normal equilibrium would consist of all kinds of ions reaching the same concentration in either solvent. The presence of a non-diffusible, or let us say, a colloidal ion in one of the solutions causes the concentration of each single

ion to become unequal in the inside and the outside solution, even in the very condition of thermodynamical equilibrium. The colloidal ions, so to speak, retain a part of the oppositely charged ions and repulse a part of the ions of the same charge through the membrane. At the same time an electrical potential difference arises between the two sides of the membrane the amount of which can be calculated by a simple thermodynamical consideration. Let us suppose that the outside solution contains sodium chloride and the inside solution a colloidal ion with a positive charge, then equilibrium is governed by the following conditions. First, the law of electroneutrality demands that within either solution the sums of the positive and of the negative ions are equal to each other. Secondly, a thermodynamic consideration demands that the product of the concentration of the sodium ions and the chlorine ions in either solution is the same. The result is that the concentration of sodium ions within the colloidal solution is smaller than in the other solution, and the concentration of chlorine ions is greater in the colloidal solution than in the other, the ratio of the sodium ion concentrations being the same but reciprocal to the ratio of chlorine ions. The potential difference of the solutions must be proportional to the logarithm of that ratio. When this ratio amounts to 1:10, the potential difference at 19° is 58 millivolts. This theory has

been experimentally confirmed by Donnan and Garner, first, for a membrane of copper cyanide and suitable electrolytes. In 1914 Procter attempted to use this theory for a theory of swelling of gelatin. He assumed a gelatin sol to contain gelatin ions which cannot diffuse into the surrounding water through the surface of the piece of gelatin. Thus this surface is equivalent to a membrane impermeable to gelatin ions, but permeable to other ions. Therefore, the Donnan laws are applicable in this case. In consequence of this law the total concentration of all ions within the gelatin is different from the one outside the gelatin, and furthermore, the osmotic pressure is different, and this difference of osmotic pressure causes the gelatin to attract water and to swell. This theory has been assumed by Jacques Loeb and led him to make a splendid series of experiments showing that generally and completely the efficiency of electrolytes in colloidal solutions may be reduced to the Donnan rule. A detailed description of Loeb's experiments would exceed the scope of these lectures. I shall confine myself to some typical points. A necessary consequence of the Donnan theory is that the effect of some ion upon any colloidal quality such as swelling, viscosity, osmotic pressure or potential difference between the particles and the solution, and hence the velocity of cataphoresis, equal conditions being given, would depend only on the *sign* and the *valency*

of the ion. Loeb has shown this to be true in very different conditions and within a rather large range of ion concentrations. Especially he proved that the apparent contradictions which would be found between this theory and the results of many other authors before, may be reduced almost entirely to an error of experiment, namely, to a neglect of measuring the pH. Loeb even emphasizes that at least in the cases investigated by him, the so called Hofmeister series of ions very often met in literature, do not hold at all. According to the Hofmeister series even equivalent ions have a different efficiency on colloidal conditions, for instance increasing in the order Li, K, Na, Rb, Cs. Without doubt Loeb has proved the truth of his opinion in all conditions studied by him. Afterwards we shall see that in *other* conditions the Hofmeister series still becomes manifest, but that does not hold in Loeb's experimental conditions. Indeed, this fact was unknown to many colloid-chemists and has to be regarded in any theory of ion effects on colloids. I wish to quote only the following order of experiments.

A solution of gelatin, a little acidulated, so that the particles of gelatin are positively charged, is separated by a collodion bag from an aqueous electrolyte solution such as sodium chloride, and the equilibrium of diffusion is observed. First the following conditions are found to be definite: the concentration of chlorine ions in the inside solution

containing gelatin is larger than in the one outside in a certain ratio; the concentration of sodium is *smaller* inside than outside, and so is the concentration of hydrogen ions. The ratio of the concentrations of hydrogen ions is the reciprocal of that of the chlorine ions. The osmotic pressure of the gelatin solution, compared with that of the outside solution by means of a rising tube, is higher in a ratio calculable from the increased ionic contents with a fair degree of accuracy. The potential difference of the solutions inside and outside is found to be that calculable from the Donnan formula. That means: the potential difference is proportional to the logarithm of the ratio of distribution of any diffusible ion, the factor of proportionality being the expected one.

In this experiment a *liquid* gelatin solution and a watery solution are separated by a collodion membrane. As long as the experiment is arranged in this way, no objection seems to be possible. Discussion only begins, when following Loeb we transfer this theory to conditions where such membranes, in the proper meaning, are no longer given. When a piece of solid gelatin is put into a salt solution, a proper membrane does not exist, of course, but the same conditions in establishing the equilibrium of diffusion are given as though there were a membrane. The particles of gelatin adhere to each other by cohesion and have no tendency to diffuse into

the watery solution. Now, the solid gelatin may be considered as a solution containing water and salts, and the Donnan theory may be applied in this case. Let us advance one more step. Let a solution of any colloidal protein be given, that means a protein substance which is not moleculary dispersed in water. In this case the particles of the colloidal solution are micellae formed by numerous protein molecules. Within these micellae the protein particles are fixed to each other by cohesion forces so as to not be able to freely diffuse into the solution. But such a micella, besides the frame of protein molecules, contains water and salts, too. Each single micella behaves as though it were surrounded by a membrane impermeable only to protein molecules. So, again, we may apply the same thermodynamical considerations as for the case of a membrane. Each kind of ion aims at a distribution between the interior of the micella and the solution, the ratio of distribution being the same for all kind of positive ions and the reciprocal one for negative ions, if all ions are univalent. If among the ions there are bivalent ions, the ratio of distribution of these is equal to the square root of the ratio of the univalent ions. The osmotic pressure within and without the micellae is different, in consequence of which an imbibition or swelling of the micellae occurs, depending on the kind and concentration of the dissolved ions, this swelling advancing to a degree, as the counteracting

force, such as the form elasticity, allows it. Thus the volume of the particles is regulated, and according to a law of Einstein, the *viscosity* of the solution depends on the volume of the particles. Furthermore, the potential difference between the micellae and the solution depends on the ratio of distribution of ions, this potential difference deciding the velocity of cataphoresis of the colloidal particles when exposed to an electrical field, according to the Helmholtz formula. It cannot be denied that Loeb has confirmed the connections postulated by the theory with a fair degree of accuracy, and slight differences might be ascribed to the fact that some of the principles of the theory only hold approximately, to which subject we shall soon return.

This theory has not been uncontradicted. Among the objections there is one which seems to me to require serious consideration.

Loeb calculates the ζ-potential, i.e., the potential which determines the velocity of cataphoresis, from the distribution of the ions on the two sides of a real or of an imaginary membrane. This distribution takes place according to certain thermodynamic laws. The potential which may be calculated from these suppositions is the potential difference between any place on the one side and any place on the other side of the membrane. It is the "thermodynamic potential" or the ϵ-potential. In my first lecture I showed that these two kinds are not

necessarily identical but that the ζ-potential may be only a part of the total potential fall from one phase to the other. The amount of the ζ-potential may be smaller than the total of ϵ-potential, and even under certain circumstances of an opposite sign, i.e., if strongly adsorbable ions are present and disturb the regular course of the potential fall. In such a case it could not be expected at all that any thermodynamic calculation would be adequate to calculate the potential which determines the velocity of cataphoresis. Though such a possibility cannot be denied, it is not necessary that under any condition the ζ-potential and the ϵ-potential are different magnitudes. If the whole fall of the potential takes place within those layers which move in cataphoresis experiments, there cannot be a discrepancy between the ζ- and the ϵ-potentials. In the absence of strongly adsorbable ions these two kinds of potential differences are probably identical. In my first lecture I mentioned the case of the potential of a mercury meniscus. In this case also most physical chemists trust the theory, that the zero point of the thermodynamic potential coincides with the maximum of surface tension, at least in absence of strongly adsorbable ions. After all, the question should be investigated once more. The problem seems to be under which conditions the discrepancy of an ϵ- and a ζ-potentials becomes manifest. It is at least very probable that the same considerations

which are valuable in the case of the mercury meniscus and have been very clearly developed by Freundlich might be applied to the case of cataphoresis. Probably the theory of Loeb has to be modified for a general application, while it is valuable in certain cases investigated by him.

However there is one question concerning this theory, that is, how to reconcile it to my former ideas, how to bring it into harmony with one of the types of potential differences mentioned above. The following consideration seems to me to be the solution of this problem. Producing a potential difference by a Donnan effect is nearly the same as producing a potential difference by a dissociation tendency. In the theory of dissociation the original supposition is that a solid particle is endowed with a dissociation tendency. This condition does not generally exist in a pure form. The micellae of a colloidal solution do not only contain that kind of molecule which embodies the colloidal behavior but also water and salts. In a pure crystal of salt the dissociation tendency of either ion may be considered to be a constant. In a real colloidal micella containing the colloid, water and salts, the dissociation tendency of the colloidal electrolyte may depend on the *concentration* within the micella of this colloid. Generally, this solution not being a dilute one but often a very concentrated one, parallelism of concentration and thermodynamical activ-

ity does not hold. In the case when the colloidal particles contain so much water that it may be considered as a dilute solution, one may use the conception of "concentration" of the molecules in the usual meaning. These conditions being given the dissociation tendency is governed by the Donnan law. For in Donnan's consideration there is the supposition that an electrolyte enclosed within a membrane has the tendency to emit one ion and not to emit the opposite ion, across the membrane. So the so-called Donnan mechanism is a limiting case of the dissociation tendency in colloids, which is available for colloidal micellae holding an abundant amount of water. The advantage of the theory of Loeb, which takes account of the thermodynamic distribution of ions, is the possibility of a quantitative examination in suitable cases. This possibility has, at least hitherto, not been applicable to the general theory of dissociation tendency.

In comparing the theory of Loeb with my system of potential differences in colloidal particles you recognize that there is neither a contradiction nor an essentially new kind of potential but only a special case.

I am conscious of the fact that this system of electrical double layers in colloidal solutions may be incomplete and perhaps partly doubtful. But you might consider it, at least, as a first attempt, and though perhaps wrong and inadequate yet useful as a fulcrum for further investigations.

VII. LYOTROPIC EFFECTS OF IONS

Hitherto all effects of ions might be reduced to adsorption in a wider meaning of the word, or at least we could start all considerations from this point of view. But there is another effect of ions which cannot be connected with any adsorption at all, because the ions producing the effect do not even combine with the substrate affected, but only influence the substrate from a distance, the solvent being a mediator of the effect. The difficulties which were for a long time an impediment to a systematic representation of ion effects were chiefly caused by the fact that the discrimination of these two kinds of effect were only very slowly and gradually developed. We may imagine the circumstances in the following manner, somewhat schematized: an electrolyte being added to a colloidal solution, the ions are partly adsorbed or fixed and so display an effect; another part remains in the solution. But this part has also an effect on the colloid by a more indirect way inasmuch as the dissolved ions enter into a competition with the colloid particles for the water placed at their disposal. We may call all effects discussed before, *direct* effects, and this new one an *indirect* effect. The direct effect may also be called the electrostatic effect,

because it is chiefly determined by the purely electrical qualities of ions, that means the sign of charge and valency; and the specific chemical qualities of ions generally do not become manifest. The indirect effect, according to Freundlich's proposal, may also be called the lyotropic effect, because it is directed to the solvent medium. This effect is not so much connected with the sign of charge, or with the valency, as it is with the so-called hydration of the ion, that is, the faculty to combine with water molecules. For a long time experiences with electrical conductivity and other qualities have led us to the idea that ions in aqueous solution combine with water molecules at a rate depending chiefly on the specific chemical nature of the ion, but secondarily also on the concentration of these ions and the presence of other ions dissolved at the same time. For instance, among the univalent alkali ions the hydration decreases with increasing atomic weight or atomic radius; the hydration diminishes according to the series: Li, Na, K, Rb, Cs. As for the nature of this combination with water molecules, different opinions arose at different times. Formerly physical chemists inclined to the idea that each ion, a sufficient quantity of water being given, is combined with a quite definite number of water molecules, just as the molecules or the ions of a crystal are combined with a definite quantity of water of crystallization, and numerous attempts

were made to determine the number of water molecules held by each kind of ion. However, different methods gave different results, only the relative position of the ions within the series was found to be nearly the same, whatever method might be applied. Thus by and by the opinion changed, and I think we should prefer the idea that hydration of ions does not mean combination with a definite number of water molecules, but a general attraction of all water molecules surrounding the ion. This representation has developed out of the atomic model of Rutherford and Bohr, and by the suggestion of Fajans and of Debye to consider the water molecules as an electrical dipole, with one end negative and the other positive. The attractive force of ions directed at water molecules surrounding them is interpreted as an electrostatic effect. A positive ion attracts water molecules in such a manner that the negative end of the water molecules approach the ion; and the water molecules polarized in this manner have a directing or polarizing influence on the more distant water molecules, decreasing with the distance. So an apparent effect at a distance on a colloid particle, by an ion, may take place, in which, however, the water molecules act as an intermediary; such an intermediary effect being the principle in each modern theory of "effects at a distance." The power of combining with water in ions carrying equal charges chiefly depends on the

distance to which the water molecules can approach the free electrical charge of the ion. For instance, in positive ions, the free charge is situated in the atomic nucleus, and the approach of the water molecules is limited by the size of the atomic radius. Therefore, hydration of positive ions decreases with increasing atomic radius.

Now, every kind of solubility means some relation of the dissolved matter to the solvent, in our cases always water. That does not only hold for true solutions but also for some colloidal solutions, namely, for those colloids which spontaneously dissolve or swell in water, such as proteins. It does *not* hold for those colloids which can be dispersed only by indirect methods, at the expense of large quantities of energy as metal sols or mastic sol. These colloids form a stable solution only when protected by an electrical double layer of a sufficient potential difference. These two groups of colloids, long known may be best distinguished in the terms of Freundlich: lyophilic and lyophobic colloids. But only in lyophilic colloids the indirect lyotropic effect of ions becomes clearly manifest. In lyophobic colloids the effect of ions is confined to the direct effect, described in the foregoing lectures. However, for lyophilic colloids, the lyotropic effect of ions intervenes, there is a competition of the lyophilic colloid and of the lyotropic ion of the added electrolyte in combining with water molecules. The two groups

of colloids not being quite distinctly separated, transitions may occur.

Of lyotropic effects there is such an abundance of phenomena that a systematic description seems to me almost impossible today. I prefer to elucidate the problem through some examples. The first one concerns the effect of different ions on the flocculation of serum albumin. When a dialysed dilute solution of albumin is boiled, a homogeneous opalescent solution results, containing denatured albumin. When a feeble acetate buffer of pH 4.7 is added, flocculation occurs; when the pH is either higher or lower than 4.7, no flocculation is to be seen. Cataphoresis experiments taught us that pH 4.7 is the isoelectric point of albumin, and so it is easily understood why pH 4.7 is the optimum of flocculation. Provided the concentration of the salts, either the salts of the buffer itself or other salts added, is very low, they have no influence and the total effect of salt can be explained by the influence of this salt on the pH. In higher concentrations the added salts bring about a double effect. First, they displace the optimum of flocculation to another pH. Strongly effective anions displace the optimum to the more acid side, cations to the less acid side as I showed some years ago. Both cations and anions may be ordered into a series of increasing effect in this regard. Most evident is the series of anions, namely, Cl, Br, I,

CNS. However, we are here chiefly interested in the second effect of ions, that is either the inhibition or the augmentation of flocculation obtainable at its optimum point. The series of anions according to increasing flocculating effect is SO_4, Cl, Br, I, CNS. The first members of the series inhibit the flocculation, the latter ones increase it. Sulfate checks flocculation so strongly that even in a small concentration flocculation is completely suppressed. Chlorine checks, too. But Br, I, and SCN accelerate and augment the flocculation. That holds in concentrations of from 0.1 to 0.5 normal. But when the concentration is higher, about 1 normal or more, the series of anions is reversed, as Labes found out in my laboratory. The sulfate flocculates most of all, and I and CNS least of all, and the Hofmeister series for albumin flocculation in weakly acid solutions becomes evident, sulfate being the best flocculating anion, I and CNS the least flocculating ones. The interpretation of these experiments seems to me to be the following. In low concentration, the effect of these ions, which are adsorbed by the protein, is prevalent and can be explained by the electrostatic effects. In high concentration the hydrophilic effect of the dissolved ions prevail. Sulfate ion attracts water molecules most of all, I and CNS least of all. So sulfate depresses the solubility of albumin most. However, this explanation does not satisfy us completely;

for experience seems to prove that I and CNS even *augment* the hydration of albumin, compared with the hydration in almost pure water. We have not yet a suitable idea of how the water-attracting property of an ion may augment the solubility of another substance, and you see we are still far from a complete theory about the hydrophilic effect.

Let us proceed now to another example, the influence of ions on the swelling of agar. Some time ago van Kruyt and de Jong drew the attention to the cololidal properties of agar and through these investigations it became manifest that this material is the prototype of a special kind of colloid, the qualities of which are very evident and comprehensive. Van Kruyt worked on the viscosity of agar; recently Dokan in my laboratory investigated the process of swelling, and I should like to describe to you his results. When a piece of agar jelly is put into water or an aqueous electrolyte solution, swelling occurs and the weight attains a constant value about after one day's swelling. The degree of swelling can be measured very exactly, and the swelling is found to be most pronounced when agar is exposed to pure water. Any electrolyte added lowers the swelling. In figures 2 and 3 the abscissa represents the negative logarithm of the concentration of the electrolyte added and the ordinate the relative degree of swelling, the swelling in pure water being taken equal to 100. So, as you see, all

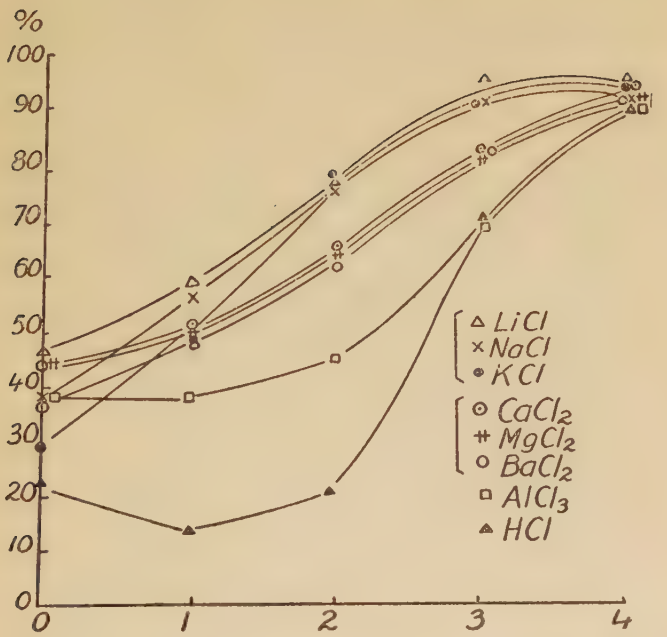

FIG. 2. Swelling of agar in solutions of chlorides of different cations.

Abscissa: Equivalent concentration of the salts.

Ordinate: Degree of swelling, in comparison to the one in pure water = 100%.

electrolytes diminish the swelling. First look at the figure 2 representing the influence of chlorides of different cations. When we first examine the lowest concentrations from 10^{-4} up to 10^{-2} normal,

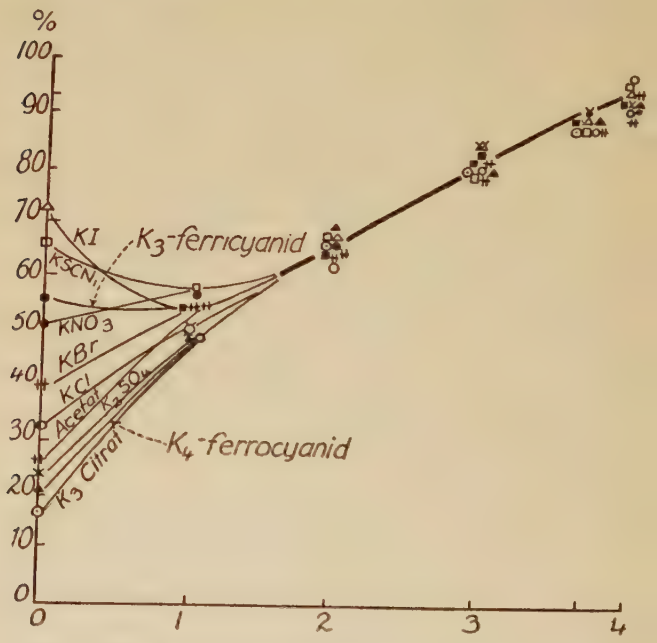

FIG. 3. The same, with potassium salts of different anions

all univalent cations form a common curve. All bivalent cations have a stronger effect and are united in another common curve, the trivalent aluminum is still more effective, and most effec-

tive of all is the hydrogen ion. In these low concentrations there is only a direct electrostatic effect exerted by the cations on the electronegative agar, depending only on the valency, save the hydrogen ions, which are superior even to trivalent ions. The results are similar to van Kruyt's on viscosity. But now look at the higher concentrations from 10^{-2} up to 1 normal. Here a divergence of the single curves takes place, the valency of the ions loses its importance, the alkali cations diverge into the well-known series Li, Na, K and so on. In these higher concentrations the primary pure valency effect of ions is overshadowed by a lyotropic effect which does not depend on valency. Now look at figure 3. Here you see the effect of potassium salts of different anions. Since agar is an electronegative colloid, anions have no direct electrostatic effect on it at all. Up to a concentration of 1/100 normal there is not the slightest difference of the effect by the different potassium salts, even polyvalent anions do not act differently from the common univalent anions, nor do hydroxyl ions either. But as soon as you proceed to higher concentrations the anions of different kind diverge and the Hofmeister series becomes manifest: citrate, sulfate, Cl, Br, SCN, iodide. In figure 4 you see the effect of different acids. The abscissa represents the concentration of hydrogen ions in the solution determined electrometrically; up to 0.1

normal of hydrogen ions there is no difference in the effect of different acids at all. Only in the highest concentrations is a divergence to be seen.

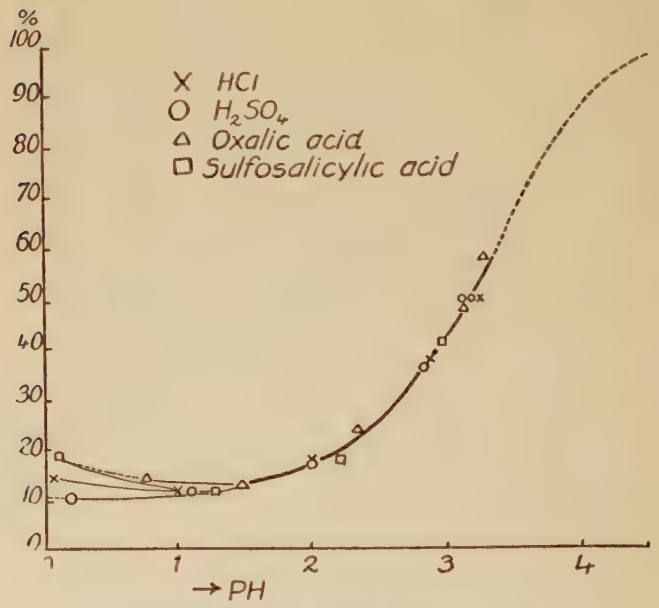

FIG. 4. Swelling of agar in different acids
Abscissa: pH
Ordinate: Degree of swelling

van Kruyt has stated that agar behaves like a hydrophobic negative colloid, but you see that for swelling, that holds only up to electrolyte concentrations of 1/100 normal, above that concentration

the hydrophilic effect of ions is developed in a very evident degree.

Now I should like to demonstrate a hydrophilic effect of a quite peculiar and strange kind. The material is a colloid which is contained in a Japanese food stuff called *Konyaku*. It is obtained from a plant very common in Japan, forming tubers like potatoes. This tuber contains a colloid substance, which Mayeda called konyaku-mannane and is said to consist of a polysacharide of mannose and glucose and perhaps partially replaces the starch of other plants. The plant is called *Amorphophallus konyaku*. After purification by repeated coagulation by alcohol one can obtain a finely granulated substance with swells enormously in water. The colloidal behavior of this substance not having yet been investigated, I asked Dr. Dokan in my laboratory to investigate the influence of electrolytes on the swelling of a jelly prepared from konyaku. The results obtained were very striking. First you see in figures 5 and 6 that any electrolyte up to a concentration of 0.01 normal, even almost up to 0.1 normal, does not influence at all the swelling in water. The line marked by 100 is the degree of swelling in pure water, and you see that neither varied cations (fig. 5) nor varied anions (fig. 6) have any effect exceeding the limits of error. There is only one exception, potassium hydroxide. It is very strange that the OH ions of this electrolyte do *not increase*

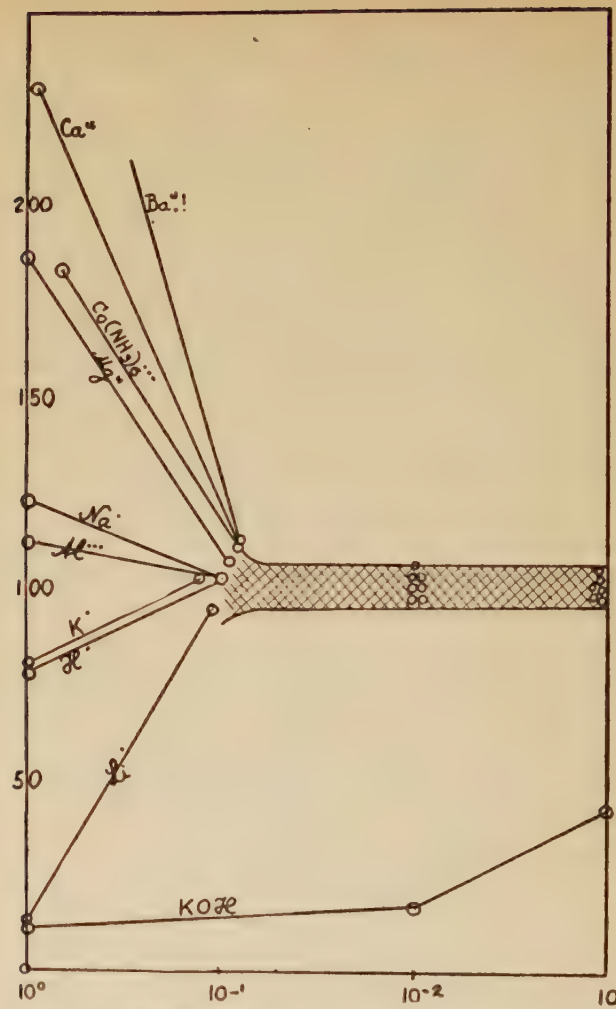

FIG. 5. Swelling of Konyaku under the influence of different chlorides. The cation is designated at each single curve. The lowest curve represents an experiment with KOH.

Abscissa: Concentration of the applied electrolyte, in negative logarithms.

Ordinate: Degree of swelling, the swelling in pure water taken = 100. The mark ! means uncertainty in weighing because of peptisation of the jelly. (From a paper by Dr. Dokan, Nagoya.)

but decrease the swelling. In concentrations as low as 0.001 normal there is a considerable diminution of swelling, and in higher concentration the

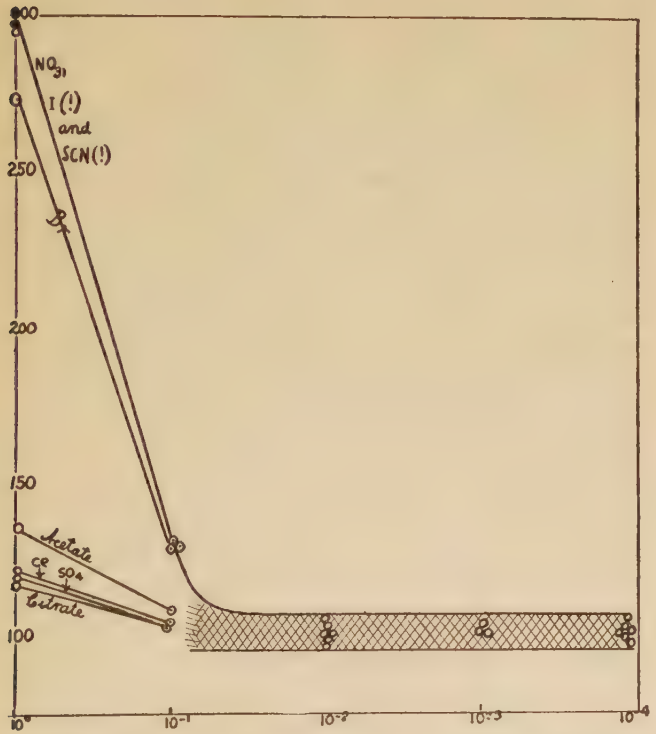

FIG. 6. The same, for potassium salts of different anions

jelly, dried before in air, almost does not imbibe water. There is no other ion having a similar effect, not even hydrogen ion, the effects of which in no

regard exceeds other ions. By proper investigations it was proved that the effect of potassium hydroxide is not caused by a chemical alteration of the colloid but by a reversible influence on the colloidal conditions. Thus you see, except for hydroxyl ions, there is no direct electrostatic effect at all in lower concentrations. But when we proceed to higher concentrations of ions you see quite an enormous effect of the different ions, even higher than in any colloid, which, however, is not ruled by the sign or the valence of the ions. In agar, all electrolytes in any event only *diminish* the swelling in comparison with pure water; in konyaku some electrolytes lower, others increase the swelling when compared with pure water. You see a large divergence of the different kinds of ions according to a Hofmeister series, as Li, Na, K, and also Cl, Br and I. The points designated by exclamation points are uncertain because in these cases, namely, in Ba, iodide and thiocyanate, the swelling proceeds so far that almost a complete dissolution or peptization of the jelly piece takes place which prevents an exact weighing. Compare with this enormous effect the effect of Li which totally suppresses the swelling. In 1*N* concentration the solid piece of jelly does not swell at all in the presence of lithium chloride or KOH. I wish to draw your attention especially to the contrary effects of lithium and barium. Such a difference cannot be explained by a direct effect

of the electrical charge of ions, but is a specific effect which we may class with the hydrophilic effects until we shall be able to differentiate these effects more accurately.

When you compare the experiments in agar and in konyaku you easily see that one cannot talk of *the* hydrophilic effect of ions. In different cases different kinds of effects become manifest, not even the series of ions always remaining the same. I might give many more examples without exhausting the subject. The obscurer a subject is the more one can talk about it, but that is not my purpose. I only wish to emphasize the remarkable contrast to the direct electrostatic effects of ions.

However one should not think that the lyotropic effect of ions is confined to the domain of colloidal substances, and it is not likely that we will attain a distinct comprehension of it before having studied these effects in simple true solutions. Therefore we ought to trace the hydrophilic effects of ions back to true solutions. I should like to show you a lyotropic effect of ions which may elucidate the general importance of these phenomena by a very simple example: the influence exerted by ions of different kind on the potential difference of a hydrogen electrode against a watery solution. According to the Nernst theory of metal electrodes, the potential difference of a platinum-hydrogen-electrode is said to depend only on the hydrogen ion concentration

of the solution which is in contact with the electrode. This theory is well known to all biologists today, the pH determination is totally based on this theory. Nevertheless, in consequence of a series of investigations of G. N. Lewis, Milner, Bjerrum, Ghosh and others, we are compelled to modify this theory. It is not the true concentration of hydrogen ions which we can determine by means of a gas chain, but the so-called activity of the hydrogen ions. The concept of activity, as first used by G. N. Lewis, means a certain function of the true concentration, which only in very dilute solutions becomes equal to the true concentration. Only in so far as the osmotic pressure is proportional to the concentration, is the true concentration of an ion identical with its activity. Now, in solutions of ions, this proportionality of osmotic pressure and concentration, as shown by van't Hoff to hold for non-electrolytes, does *not* hold even in rather low concentrations. All former methods of determining the true concentration of ions in solution of strong electrolytes have become doubtful. Especially, those data obtained by measuring the electrical conductivity or by the determination of the freezing point, are surely erroneous. For instance, determination of conductivity and freezing point appeared to prove that hydrochloric acid or potassium chloride are only partially dissociated in aqueous solutions. Today it has become certain that the dis-

sociation must be much higher than such a calculation seems to prove. We are justified in considering all so called strong electrolytes as being practically totally dissociated under any conditions of concentration. But neither the determination of the electrical conductivity, nor of the freezing point, nor even of the potential difference against a suitable electrode directly informs us about the true concentration of ions, but only about a certain function of this concentration, which is not even the same for all of these three methods. *That* function of concentration obtained by calculation from the potential according to the Nernst formula has been called the *activity* of ions, and this activity is, for chemical applications, still more important than the true concentration, because this activity is the same activity that has to be applied in the law of mass action in chemical reactions, instead of true concentrations. The concept of this activity is necessary for all thermodynamic considerations of solutions.

Now, let us take a 0.01 normal solution of hydrochloric acid, and add neutral salts of different kind and concentration. When we measure the potential difference of these solutions against a hydrogen electrode, the potential varies according to the added salt. If we would apply the original theory of Arrhenius, an added neutral salt should only diminish the degree of dissociation of hydrochloric acid and so diminish the hydrogen ion concentration too.

But experience shows the contrary as a rule, as shown by several authors during the past decade. The difficulties of these investigations were always the elimination of diffusion potentials. By means of a special method elaborated for this purpose in my laboratory, Dr. Mizutani and I obtained the following results (see fig. 7). In each single experiment we measure the potential of an 0.01 normal hydrochloric acid against a hydrogen electrode. The solution, besides this acid, contains a neutral salt in a concentration marked on the abscissa. The ordinate, when reading it at the scale of the right-hand side, shows the potential difference against a hydrogen electrode, the potential of the salt-free acid solution being set equal to zero; when you read the scale of the ordinate at the left-hand side, you have the difference of pH in comparison with the pH of the salt-free acid solution, calculated from the potential by means of the Nernst formula. As you see, only in rather low concentrations of salts is the acidity of the solution lowered by salts, as must be expected in any concentration, if the original theory of Arrhenius holds. But generally, in any higher concentration of any salt, on the contrary, the acidity *increases* in presence of salts. When cations are varied, comparing the effect of chlorides of different cations, you may see the well-known lyotropic series: Li, Na, K, Rb. When looking at the bivalent ions, you cannot generally see a higher

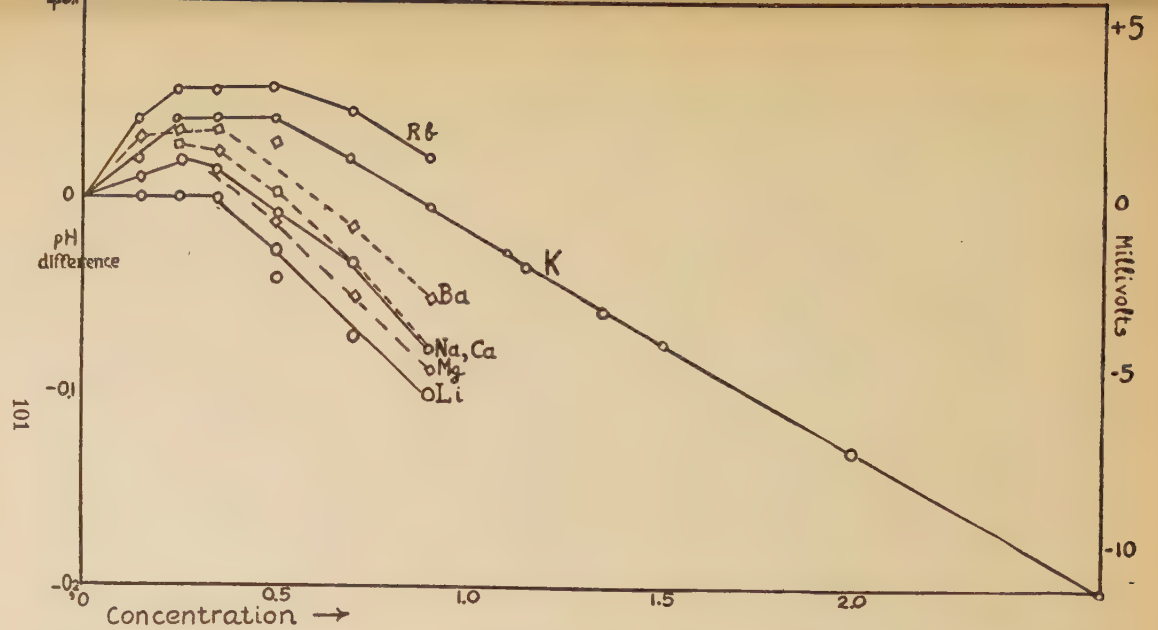

FIG. 7. The potential difference of 0.01 N HCl solution against a hydrogen electrode is measured. The HCl solution contains neutral salts of different kind, in form of the chlorides of different cations designated at the curves, and in a concentration designated in the abscissa. The left-hand scale of the ordinate gives the difference of the pH and the pH of a salt-free 0.01 N HCl solution, calculated by means of the Nernst formula. The right-hand scale of the ordinate is the potential difference in millivolts, the potential of the salt-free solution taken = 0. (From Michaelis and Mizutani.)

efficiency, but bivalent ions are interpolated between Li and Rb. The valency rule becomes invalid, lyotropic properties preponderate. You may comprehend this effect by the following image. The potential of a hydrogen electrode is the sum of two magnitudes: first, the electrolytic solution tendency of Nernst. Let us consider it as a constant. Second, the counterpressure of the dissolved hydrogen ions, which tends to push the dissolved hydrogen ions into the electrode. This counteraction is weakened by the attraction of the water molecules exerted on the hydrogen ions dissolved. When you add ions which can attract water molecules, the attraction of water molecules and hydrogen ions is diminished, and the counteraction of the dissolved hydrogen ions against the electrolytic tendency of the electrode is augmented, the solution appears to behave as one which has become more acid. From this we may infer that the apparent augmentation of acidity produced by an ion is the stronger the higher the hydration of this ion. Indeed, you see this suggestion confirmed by the experiment. The feebly hydrated rubidium acidifies the solution least, and the highly hydrated lithium acidifies most of all the alkali ions. Sometimes the effect is very considerable. Thus a 0.01 normal solution of hydrochloric acid, when a 2.7 normal solution of potassium chloride is the solvent, appears to contain a hydrogen ion concentration of about 0.017 normal, which is

mere nonsense from the standpoint of the former theory of electrodes and dissociation.

From this example you may see that the hydrophilic effect of ions is widely spread even in common true solutions, and however important these effects may be for biologists, successful work on biological subjects cannot be started before the principles are established for simple inorganic substances.

VIII. MIXTURES OF ELECTROLYTES

Hitherto we always took into consideration the effect of a single kind of ion. Let us finally examine mixtures of electrolytes. When two ions of equal charge are mixed and the influence on the condition of a colloid is compared with that of either ion alone, two possibilities may occur. Either the effect is a kind of summation, or an antagonistic effect is to be seen. As a rule summation occurs; antagonism is rarer in inanimate systems, but in living matter antagonism is very common and appears to be one of the most important principles which regulate the colloidal behavior of cells. Ringer pointed out that pure NaCl, even in isotonic solution, acts as a poison on frog muscles, enormously increasing the irritability, and $CaCl_2$ in a very small amount annuls this poisonous effect. As Jacques Loeb found, a similar antagonism between univalent and bivalent cations takes place in the development of fertilized eggs of *Fundulus heteroclitus*, and since that time numerous cases of ion antagonism have been described in living cells in such a degree that the mutual relation of different ions in the liquids of living organisms is supposed to be a most important regulator for normal cell functions. The mechanism of this antagonism is an urgent problem for investi-

gation. Let us discuss what we know about the effect of ion combinations in inanimate systems. I think we are justified in setting up the following thesis: in those cases where the direct electrostatic effect of ions occurs and the valency rule holds and other chemical specificities are insignificant, only a summation of ion mixtures is to be observed; antagonism never occurs. For instance, consider the flocculation of a mastic sol by a mixture of hydrochloric acid and $CaCl_2$. A concentration of HCl which of itself is insufficient for flocculation can be rendered effective when a small amount of $CaCl_2$ is added which alone is not sufficient for flocculation. This may be expected and is not surprising, and I need not illustrate this point by more examples.

But also in cases of lyotropic effects where the valency rule does not hold, and the Hofmeister series becomes evident, summation effects are usual, for inanimate systems. A very striking example which has been investigated recently by me and Mizutani is the combination of two cations added to a 0.01 normal HCl and measuring the potential difference against a hydrogen electrode. The effect of the mixture is always exactly a summation of the single effects. When one applies KCl in the concentration A and $CaCl_2$ in the concentration B in a mixture, the effect on the pH is the same as though you had applied $CaCl_2$ first in such a concentration as to be of equal effect to KCl in the

concentration A and moreover had added the amount B of $CaCl_2$.

In some cases of lyotropic effects on inanimate models, however, antagonism can be shown. It is strange that such cases are so rare. For the first time Linder and Picton observed an antagonism of univalent and bivalent cations in the coagulation of arsenic sulfid sol. Then Sven Odén found a new case in sulfur sol, which recently has been accurately investigated by Freundlich and Scholtz. Sulfur sol may be made in two different ways. The sulfur sol of v. Weimarn is made by mixing an alcoholic sulfur solution with water. This colloid is a decidedly hydrophobic one and no trace of ion antagonism can be seen in it. The sulfur sol of Odén is obtained when H_2S is led into sulfurous acid. This is a decidedly hydrophilic sol, much less sensitive to electrolytes, and reversible. In this sol the antagonistic effect of univalent and bivalent cations may be easily observed, the most evident antagonism is the one between Li and Mg. Also some other cases have been described in the literature, but they are mostly doubtful. I can relate a new case which I asked Dr. Minakami to investigate in my laboratory, that is the effect of electrolytes on a solution of soap or sodium oleate. Soap gives a colloidal solution in water the properties of which have best been investigated by MacBain. It has been known for a long time that electrolytes change the colloidal

condition of soap solutions; they first increase the opacity and then bring about flocculation. Bivalent ions such as calcium are much more effective than univalent ions. But within the series of univalent ions there are considerable differences of effectiveness. Now, when to a watery soap solution an amount of NaCl is added sufficient to bring about a strong opacity and then there is added a small amount of $CaCl_2$, the opacity does not become stronger but weaker. This antagonism can be seen between Na, K or Li on the one side, and Ca or Mg, and Ba and Sr to only a slight degree on the other side. In soap solutions this antagonism can also be observed in the effects on surface tension, though in a much lower degree, most remarkably shown in Mg and Li, much less in Ca and Na. But experiments with opacity are most evident and very striking. But in this case it becomes quite evident that the word antagonism is not wholly adequate; the observations show the following details as pointed out by Dr. Minakami in my laboratory. A pure aqueous soap solution has a certain weak opacity. When you add even a small amount of lithium chloride or a similar salt, the opacity becomes much stronger, even without real coagulation and sedimentation taking place. The solution loses its transparency. Now when you add a small amount of $CaCl_2$ a quite new situation arises. The effect of calcium is not simply a counteraction against the

lithium effect. For when the concentration of Li is diminished in absence of calcium, one can never obtain a similar condition of opacity. An opacity produced by Li alone even in smallest concentrations is always coarse-grained and opaque. When Ca is added, according to the conditions, the opacity may perhaps also appear strong when observed from the side with the Tyndall beam; but when observed in transmitted light, the solution appears quite transparent. The colloidal condition is altered throughout, and a new condition of dispersion is brought about which cannot be attained by either component of the mixture in any concentration. This fact seems to be analogous to the observations on living matter. In frog muscle preparations when $CaCl_2$ is added to NaCl, the conditions of pure distilled water or isotonic sugar solution are not restored either, but a new condition arises. The mixture can by no means be wholly replaced by any simple solution. So it is in soap solution, likewise, and this is the best model of ionic antagonism comparable with living matter. But as for a physicochemical theory of this effect, it must be postponed for the present, because adequate models for physicochemical experiments are still lacking. This one point only may be considered as certain, that this phenomenon never occurs as a result of purely electrostatic effects of ions, but only in lyophilic colloids.

Sans Tache

Sans Tache

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